Sub-molecular details in the STM imaging of 4-nitrophenyl thiolate self-assembled monolayers

by

Goli Pourmand

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ABSTRACT

SUB-MOLECULAR DETAILS IN THE STM IMAGING OF 4-NITROPHENYL THIOLATE SELF-ASSEMBLED MONOLAYERS

Goli Pourmand
University of Guelph, 2018

Advisor:
Dr. Aziz Houmam

Self-assembled monolayers (SAMs) on solid surfaces and in particular aromatic SAMs, attracted considerable attention in recent years due to their unique electrical properties. Low packing density and irreproducibility are common problems associated with aromatic SAMs. In this study, a wide range of modification conditions were used to achieve high coverage SAMs for two common aromatic precursors, 4-nitrothiophenol and bis(4-nitrophenyl) disulfide. Characterization of the SAMs prepared from 4-nitrothiophenol using a number of techniques including scanning tunneling microscopy (STM) demonstrated the formation of highly packed aromatic SAMs along with observation of distinct superstructures on gold that with further analysis revealed the ability of STM to image sub-molecular details of molecules. SAMs prepared from the disulfide lead to a chemically similar monolayer but revealed a much lower coverage with no superstructures. Our results show that these distinct features are most likely induced by SAM stress and the molecules which are involved in making these structures are in a frozen state allowing for the sub molecular details to be observed by STM.
DEDICATION

This thesis is dedicated to my husband Sasan and my lovely daughter Diana
ACKNOWLEDGEMENTS

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# TABLE OF CONTENTS

Abstract ........................................................................................................................................... ii
Dedications ....................................................................................................................................... iii
Acknowledgements ........................................................................................................................ iv
Table of contents ............................................................................................................................ vi
List of figures ................................................................................................................................... ix
List of abbreviations ....................................................................................................................... xiii

**Chapter 1. Introduction**

1.1 Motivation ............................................................................................................................... 1
1.2 Objectives of Thesis ............................................................................................................. 2
1.3 Scope of Thesis ....................................................................................................................... 3

**Chapter 2. Literature Review**

2.1 General Background ............................................................................................................. 5
2.2 Langmuir-Blodgett Technique ............................................................................................ 6
2.3 Self-Assembled Monolayers (SAMs) .................................................................................. 7
2.4 Organosulfur Self-Assembled Monolayers (SAMs) on Gold ............................................ 9
   2.4-1 Self-Assembled Monolayer Structure ......................................................................... 9
   2.4-2 The Growth of SAM on Gold ................................................................................... 11
   2.4-3 Mechanism of Formation of Organosulfur SAMs on Au ................................... 13
   2.4-4 Experimental Factors Influencing the Formation of Thiolate SAMs ........... 16
   2.4-5 The Au(111) Surface ............................................................................................... 18
   2.4-6 Low and High Coverage Structures of Organosulfur SAMs on Au(111) ........ 19
2.4-7 Dynamics ......................................................................................................... 21
2.4-8 Characterization of Defects on SAMs .......................................................... 22
2.4-9 Aromatic Organosulfur SAMs on Au ......................................................... 23
2.4-10 STM Imaging of Organosulfur SAMs ....................................................... 25

Chapter 3. Materials and Experimental Techniques

3.1 Chemicals ........................................................................................................ 28
3.2 Glassware ....................................................................................................... 28
3.3 Experimental Techniques ............................................................................. 28
  3.3-1 Cyclic Voltammetry .................................................................................. 29
  3.3-2 X-ray Photoelectron Spectroscopy (XPS) ............................................... 33
  3.3-3 Polarization Modulation Infrared Reflection Absorption Spectroscopy .... 37
  3.3-3a Infrared Spectroscopy ............................................................................ 37
  3.3-3b Principals of PM-IRRAS ....................................................................... 38
  3.3-4 Scanning Tunneling Microscopy ............................................................... 43
    3.3-4a Introduction ........................................................................................ 43
    3.3-4b Principle of Operation ......................................................................... 44
    3.3-4c Operation Modes of STM ................................................................. 46
    3.3-4d Calibration of STM ........................................................................... 48

Chapter 4. 4-Nitrothiophenol and Bis (4-nitrophenyl) Disulfide as Precursors for Modification of Gold

4.1 Preparation of Au(111) on Mica ................................................................... 49
4.2 STM Tip Preparation ..................................................................................... 51
4.3 Nitrothiophenol as a Precursor for the Modification of Gold Surfaces ......... 52
  4.3-1 Stripping CV Results ............................................................................. 52
4.3-2 XPS Characterization ............................................................... 56
4.3-3 PM-IRRAS Characterization .................................................. 58
4.3-4 STM Investigation ................................................................. 60
4.3-4a Superstructures and their Dynamics ..................................... 63

4.4 Bis(4-nitrophenyl) Disulfide as a Precursor for the Modification of Gold Surfaces
........................................................................................................... 73
4.4-1 Stripping CV Results ............................................................... 73
4.4-2 XPS Characterization ............................................................... 75
4.4-3 PM-IRRAS Characterization .................................................. 76
4.4-4 STM Investigation ................................................................. 77

Chapter 5. Summary and Future Work

5.1 Summary and Conclusion .......................................................... 79
5.2 Future Work ............................................................................... 81

References ......................................................................................... 83
LIST OF FIGURES

**Figure 2-1.** Scheme of Langmuir–Blodgett (left) and Langmuir–Schaefer (right).

**Figure 2-2.** Schematic diagram showing the constituents of a SAM-molecule.

**Figure 2-3.** a) Scheme of an adsorbed alkanethiol molecule on Au(111) in close-packed structure. b) Schematic diagram illustrating the view of an all-trans conformer of individual alkanethiol molecule on a surface. (Adapted with permission from reference 12)

**Figure 2-4.** STM image of herringbone reconstruction pattern of bare Au(111). (Reprinted with permission from reference79)

**Figure 2-5.** Proposed structural models for the (√3 x √3)R30° structure and c(4√3 x 2√3) structures on Au(111). (Adapted from reference 85).

**Figure 2-6.** Schematic representation of possible SAM defects. a) Missing row. b) Vacancy islands. c) Domain boundaries. d) Molecular defects.

**Figure 2-7.** Proposed models for the formation of vacancy islands and adatom in (up) aliphatic and (down) aromatic SAMs on Au(111). (Adapted from reference 98).

**Figure 3-1.** Potential – time excitation signal in cyclic voltammetry experiment.

**Figure 3-2.** Voltammogram of a single electron oxidation-reduction.

**Figure 3-3.** Thiolate SAM formation from thiols and disulfides.

**Figure 3-4.** Schematic diagram illustrating the photoemission process.

**Figure 3-5.** Basic components of a monochromatic XPS system.

**Figure 3-6.** Illustration of the phase shift of the electric field vector for a) s-polarized and b) p-polarized radiation upon reflection at an air/Au interface.

**Figure 3-7.** Schematic showing the image effect for the metal surface.
Figure 3-8. Basic components of the STM.

Figure 3-9. Schematic figure showing tunneling phenomenon between two metals.

Figure 3-10. Modes of STM Operation: a) constant current and b) constant height.

Figure 3-11. Constant - current STM image of HOPG a) 6 x 6 nm².

Figure 4-1. Topographic images of thin gold films on mica prepared by MIDAS. (a) 800 x 800 nm², (b) 5 x 5 nm². Tip bias = +0.2 V, tunneling current = 0.8 nA, and scan rate 4.8 lines/s.

Figure 4-2. The basic tip preparation set up.

Figure 4-3. Time dependent cyclic voltammetry, in a 0.5 M aqueous KOH solution at 25 ºC, of a 2-mm diameter solid gold electrode modified with 4-nitrothiophenol.

Figure 4-4. Time dependent coverage of the monolayer deposition calculated from the reductive stripping voltammetry of previously modified polycrystalline solid gold electrodes in a 0.5 M aqueous KOH solution at 25 ºC.

Figure 4-5. XPS spectra of the sulfur, nitrogen and carbon regions of modified Au(111) on mica using a 10 mM solution of 4-nitrothiophenol in dry, degassed DMF for 48 h.

Figure 4-6. PM-IRRAS spectrum of modified Au (111) on mica using a 10 mM solution of 4-nitrothiophenol in DMF for 48 hours. b and c) Representation of atomic displacements (black arrows) and IR vectors (red arrows) of optimized structure of 4-nitrothiophenol: vibrational modes of the symmetric (b) (r+ NO₂) and asymmetric (c) (r- NO₂) stretch modes of the NO₂ group.

Figure 4-7. STM images of a Au(111) surface in air, modified using 4-nitrothiophenol (10 mM in DMF) for 48 h. (a) 30 x 30 nm² and (b) 12 x12 nm². Tip bias = 0.1 V, tunneling current (0.1 - 0.4 nA) and scan rate (4.8 lines/s).

Figure 4-8. STM images of a Au(111) surface in air, modified using 4-nitrothiophenol (10 mM in DMF) for 48 h. (a) 12 x 12 nm², (b) 3 x 3 nm², (c-d) Height profiles along line A and B. Tip bias = 0.1 V, tunneling current = 0.2 nA and scan rate = 4.8 lines/s.
Figure 4-9. a) STM image of a Au(111) surface modified using 4-nitrothiophenol (10 mM in DMF) for 48 h, 12 x 12 nm$^2$. Tip bias = +0.1 V, tunneling current = 0.2 nA and scan rate = 4.8 lines/s. (b) Line profiles along lines A, B and C over a brighter spot from three different directions.

Figure 4-10. Consecutive STM imaging of a SAM of 4-nitrothiophenol on Au(111). 12 × 12 nm$^2$. Images are taken in the sequence a-d. Tip bias = +0.1 V, tunneling current = 0.2 nA and scan rate = 4.8 lines/s.

Figure 4-11. STM image of a Au(111) surface modified using 4-nitrothiophenol showing a hexagon structure. Scan size: (3 x 3 nm$^2$). (b) to (g) Line profiles along six edges of the hexagon as marked in a.

Figure 4-12. a) STM images of a SAM of 4-nitrothiophenol on Au(111). 12 × 12 nm$^2$. b) Height profile along line A. c) optimized structure of p-nitrophenyl thiolate along with its top view. d) STM image showing a hexagon (scan size: 3 × 3 nm$^2$). e) Schematic representation of the molecular rearrangement providing the hexagonal structure. (Reprinted with permission from reference 2). f) Top view schematic structure of 4-nitrophenyl thiolate molecules on the Au(111) surface. Tip bias = +0.1 V, tunneling current = 0.2 nA and scan rate = 4.8 lines/s.

Figure 4-13. a) STM images of a Au(111) surface modified using 4-nitrothiophenol showing two parallelogram structures. d-g) Line profiles along the parallelogram edges. b) Schematic representation of the molecular rearrangement providing the parallelogram structure. (Reprinted with permission from reference 2). c) Top view schematic structure of 4-nitrophenyl thiolate molecules on the Au(111) surface. Tip bias = 0.1 V, tunneling current = 0.2 nA and scan rate = 4.8 lines/s.

Figure 4-14. Time dependent cyclic voltammetry, in a 0.5 M aqueous KOH solution at 25 ºC, of a 2-mm diameter solid gold electrode modified with bis(4-nitrophenyl) disulfide.

Figure 4-15. Time dependent coverage of the deposited monolayer calculated from the reductive stripping voltammetry of previously modified polycrystalline solid gold electrodes in a 0.5 M aqueous KOH solution at 25 ºC.
Figure 4-16. XPS spectra of the sulfur, carbon and nitrogen regions of Au(111) on mica modified using a 10 mM solution bis(4-nitrophenyl) disulfide in dry, degassed DMF for 48 h under nitrogen atmosphere.

Figure 4-17. Unfiltered STM images of a Au(111) surface in air on mica modified using bis (4-nitrophenyl) disulfide (10 mM in DMF) for 48 h. (a) 40 × 40 nm², b) 9 × 9 nm², c) Proposed structural model for the 4-nitrophenylthiolate SAM on Au(111). Bias (0.1 V) tunneling current (0.8 nA) and scan rate (4.8 lines/s).
## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>B3LYP</td>
<td>Becke, three-parameter, Lee-Yang-Parr</td>
</tr>
<tr>
<td>BT</td>
<td>Benzenethiol</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>EC</td>
<td>Electrochemical</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>fcc</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GIXD</td>
<td>Grazing Incidence X-ray Diffraction</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal closed packed</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LB</td>
<td>Langmuir-Blodgett</td>
</tr>
<tr>
<td>LS</td>
<td>Langmuir-Schaefer</td>
</tr>
<tr>
<td>LZT</td>
<td>Lead Zirconium Titanate</td>
</tr>
<tr>
<td>LBH</td>
<td>Local Barrier Height</td>
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<tr>
<td>LDOS</td>
<td>Local Density of States</td>
</tr>
<tr>
<td>MCT</td>
<td>Mercury Cadmium Telluride</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<td>--------------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>OCT</td>
<td>Octanethiol</td>
</tr>
<tr>
<td>PEM</td>
<td>Photoelastic Modulator</td>
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<tr>
<td>PVD</td>
<td>Physical Vapour Deposition</td>
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<tr>
<td>PM</td>
<td>Polarization Modulation</td>
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<tr>
<td>PM-IRRAS</td>
<td>Polarization Modulation Infrared Spectroscopy</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
</tr>
<tr>
<td>SECM</td>
<td>Scanning Electrochemical Microscopy</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning Probe Microscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>SHG</td>
<td>Second Harmonic Generation</td>
</tr>
<tr>
<td>SAMs</td>
<td>Self-Assembled Monolayers</td>
</tr>
<tr>
<td>SFG</td>
<td>Sum Frequency Generation</td>
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<tr>
<td>SPR</td>
<td>Surface Plasmon Resonance</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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Chapter 1. Introduction

1.1 Motivation

Scanning probe microscopy techniques, particularly scanning tunneling microscopy (STM), have been used extensively to investigate the morphology of self-assembled monolayers (SAMs) and to determine the molecular arrangement of adsorbates on solid surfaces. STM provides topographic images of structures on the surface that allows for determination of several properties of the SAMs including coverage, uniformity, defects, adsorption sites, etc. Despite these great uses, the information obtained by STM is still elusive. In particular the origin of the observed structures and contrasts have not been fully understood and several outstanding questions such as: What is actually being imaged by STM? (the terminal, S head group or molecular backbone), is STM able to show sub-molecular details of the molecules? remain to be answered.

There have been a few attempts to address some of these questions for example, constant-height STM of aliphatic SAMs by Zeng et al. revealed variations in the shape and brightness of the adsorbed molecules with changing the bias voltage.\(^1\) It was concluded that, surface topography dominates the STM images by demonstrating the ability of STM to image the terminal group of SAM. STM studies of 4-nitrophenyl thiolate SAMs on Au(111) in the Houmam group is another example that provided interesting insights into the nature of the bright spots observed in STM imaging and their relation to the imaged structure.\(^2\) The SAMs were obtained through use of 4-nitrophenyl sulfenyl chloride as a precursor and the STM images showed sub-molecular details that have not been reported previously. It was suggested that both oxygen atoms of the terminal nitro group of the precursor molecules were visualized by STM. This is an indication that the STM tip is in principle capable of providing the structural details of
the terminal group. Despite this strong proof of principal, the ability of the STM to uncover the sub-molecular details of SAMs still remains elusive.

The idea of the present study is to use different precursors to generate similar nitophenyl thiolate SAMs on gold surfaces. The two precursors to be investigated are the 4-nitrothiophenol and the bis(4-nitrophenyl) disulfide. Some main questions we are hoping to answer include whether these precursors can form high coverage SAMs on gold surfaces comparable to what was obtained using the 4-nitrophynyl sulfenyl chloride and whether the STM images of the SAMs obtained using these precursors show the same very unique hexagonal features corresponding to sub-molecular structures observed for the sulfenyl chloride SAMs.

1.2 Objectives of Thesis

The overall goals of this study are to produce high coverage aromatic SAMs and provide fundamental insight into the STM ability to image the end group of nitro terminated aromatic SAMs at atomic resolution by investigating the origin of the various features and contrasts obtained in STM images. Aromatic SAMs attracted considerable attention because of their unique properties that make them desirable for molecular electronics. Obtaining long-range ordered aromatic SAMs are far more challenging compared to aliphatic SAMs. Thus, we are yet to overcome the limitations including short range SAMs with inferior quality, low packing densities and irreproducibility that are generally encountered with aromatic thiols that also undergo oxidation to disulfides and sulfonates in solution.

In this study, a wide range of modification conditions have been used to achieve high coverage SAMs from 4-nitrothiophenol and bis(4-nitrophenyl) disulfide on Au (111), and subsequently a number of techniques including CV, XPS, PM-IRRAS and STM have been
employed to characterize the produced SAMs. STM was used to obtain high resolution
topographic images of the obtained SAMs in order to determine the coverage and arrangement of
the molecules on the gold surface and to understand the origin of contrasts observed in high
coverage SAMs.

The main goals of this study are:

1) To achieve high coverage SAMs using 4-nitrothiophenol and bis (4-nitrophenyl) disulfide
   as precursors on Au (111) surface under a wide range of modification conditions.
2) To characterize the nitrophenyl thiolate SAMs on Au (111) using techniques including
   CV, XPS, PM-IRRAS and STM
3) To provide more evidence into the poorly understood origin of the various structures and
   variation in brightness obtained in STM images of SAMs
4) To demonstrate the ability of the STM to capture sub-molecular details of standing up
   nitrophenyl thiolate SAMs on Au(111).

1.3 Scope of Thesis

This thesis contains five chapters. Chapter one outlines the motivations of this work and
highlights its major goals. Chapter two provides an in-depth literature review into the area of
organic thin films and in particular, self-assembled monolayers on gold, their characteristics in
terms of mechanism, growth, interfacial properties and finally interpretation of STM images of
organosulfur SAMs. Chapter three describes chemicals, sample preparation and the experimental
techniques used throughout this work. Chapter four presents the findings with regard to the
aromatic SAMs formation on Au surfaces using 4-nitrothiophenol and bis(4-nitrophenyl)
disulfide as precursors. For surface characterization, techniques including STM, XPS, PM-
IRRAS and CV are used. In the context of this thesis, a monolayer (ML) is the number of molecules per gold atom. Chapter five presents a summary and future directions of this work.
Chapter 2. Literature Review

2.1 General Background

Self-assembled monolayers (SAMs) were subject to extensive studies in the last three decades due to their wide potential range of applications, their well-defined structures, and the ease of their fabrication. The history of SAMs goes back to the observation reported by the Roman philosopher Pliny the Elder in 78 AD describing the effect of oil on water. He noticed that the sailing of a ship is different when water is covered with greasy material. This simple observation inspired many scientists later such as Benjamin Franklin, Lord Rayleigh, and Agnes Pockels. A series of experiments were performed such as spreading oil on a pond, calculating the thickness of the oil layer and developing a technique to measure the surface tension of surfactant films on water. These studies on thin films, set the stage for Irving Langmuir and Katharine Blodgett to successfully develop the Langmuir–Blodgett (LB) film by collecting amphiphilic molecules (i.e fatty acids) on the water surface. Langmuir and Blodgett received the Nobel Prize in chemistry in 1932 for their outstanding work in surface chemistry. Their work has been then followed by Zisman who pioneered the self-assembly monolayer field and made a significant contribution in this area. From Zisman work, in the late 1970s, Sagiv, successfully deposited organosilanes onto SiO₂, Si, Ge and ZnSe surfaces. Subsequently in the early 1980s, Nuzzo & Allara prepared monolayers of alkanethiolates on gold by adsorption from dilute solutions of n-alkyl disulfides which then became the most popular SAM system and brought SAMs into the mainstream scientific consciousness. Scientific interest in monolayer films soared since then and revolutionized the field of organic thin films. Self-assembly and Langmuir methods have been routinely used for the fabrication of thin films on various substrates.
2.2 Langmuir-Blodgett Technique

The method of forming thin films was developed by Irving Langmuir and his assistant Katharina Blodgett in the 1930s. When amphiphilic molecules arrive at the air/water interface, molecules orient with their hydrophilic headgroup to the water while the hydrophobic head pointing into the air. Later, these films were deposited on a solid surface by dipping a solid substrate into the liquid with a constant speed. A monolayer with very accurate thickness was adsorbed homogeneously with each immersion and repeated immersion result in the formation of a multilayer. The stability as well as the efficient packing of the LB films depend on the strength of the intermolecular interaction between adjacent molecules in the layer. A similar methodology adapted from the LB procedure is the Langmuir-Schaefer (LS) technique, where horizontal lifting achieves the deposition. Figure 2-1 shows the experimental set up for the deposition of Langmuir, LB and LS films.

While these techniques are simple, they lead in general to the formation of films with low mechanical and chemical stability. Post preparation via transfer of preassembled monolayers to the substrate also lead to instability in the monolayer. Self-assembly is an alternative technique and will be discussing in more details in the following part.
2.3 Self-Assembled Monolayers (SAMs)

SAMs are simple to obtain and are useful in tailoring the interfacial properties of semiconductors and metals. The principle of the formation of self-assembled monolayers involves the spontaneous adsorption of molecules from a liquid or a gas phase on a solid substrate or liquid surfaces to form organized monomolecular layers which result in crystalline or semi-crystalline structures.\textsuperscript{13}

The surface on which a SAM forms is referred to as a substrate and the choice of the substrate depends on the downstream applications of the SAMs and the techniques used to characterize the obtained films. The surface can be a flat surface such as silicon, glass or Mica; or highly curved nanostructures such as colloids, nanocrystals. Flat substrates are extensively used because they are cheaper and compatible with a number of surface analysis techniques.\textsuperscript{13}

The most common flat substrates for alkanethiol SAMs are thin films of metals such as gold deposited on silicon wafers, glass or mica.\textsuperscript{14,15} Amongst them freshly cleaved mica support
is easier to produce without the need for the primer layer and is compatible with more surface analysis techniques.\textsuperscript{16,17}

Several methods have been used to prepare the thin film of metals such as physical vapor deposition (PVD) methods\textsuperscript{18} and electro-deposition.\textsuperscript{19} PVD is by far the most commonly used method in the field.

SAMs of organosulfur compounds are formed, most commonly on wide range of thin film metals including coinage metals (Au, Ag, Cu), palladium, platinum, nickel and alloys.\textsuperscript{13} Silver and copper are the most studied substrates after gold, but they oxidize readily in air, so the surfaces of these metals become rougher and more heterogeneous with extended exposure.\textsuperscript{20,21} Gold on the other hand has several characteristics that makes it favorable to be used as a substrate for studying SAMs. Preparation of flat thin films of gold can be achieved by different methods including physical vapor deposition, sputtering or electrodeposition. It is easy to handle the gold samples under atmospheric conditions, because gold is an inert metal, and does not react with most chemicals.\textsuperscript{22} Using anchoring molecules with different head groups, various SAMs have been prepared and characterized, for example organosilanes (alkyltrichlorosilanes, alkylalcoxyisilanes, alkylaminosilanes) on SiO\textsubscript{2}/Si,\textsuperscript{23} Al\textsubscript{2}O\textsubscript{3}/Al,\textsuperscript{24,25} glass,\textsuperscript{26} mica,\textsuperscript{27} hydrocarbons on silicon\textsuperscript{28} and organosulfur compounds on clean metals.\textsuperscript{9,29}

Because of the high affinity of sulfur to gold, compounds with a sulfur-containing head group constitute the major class of self-assembled films.\textsuperscript{22,30} The most important SAMs, are those of alkanethiols,\textsuperscript{29} organic thiocyanates\textsuperscript{31,32} and other sulfur containing compounds, like dithiols,\textsuperscript{33} disulfides\textsuperscript{9} and sulfides\textsuperscript{34} with both aliphatic and aromatic molecular backbones.
2.4 Organosulfur Self-Assembled Monolayers (SAMs) on Gold

2.4-1 Self-Assembled Monolayer Structure

The self-assembled monolayers precursors consist typically of three components, the head group, the molecular backbone, and the end group or surface-active group (Figure 2-2). The self-assembled monolayers precursors consist typically of three components, the head group, the molecular backbone, and the end group or surface-active group (Figure 2-2).

![Figure 2-2. Schematic diagram showing the constituents of a SAM-molecule.](image)

The head group is mostly sulfur because of high affinity of sulfur on noble metals. The molecular backbone of the precursor determines the SAM structure, the thickness and the electronic conductivity. The interactions between the backbone chains (van der Waals, dipole or π-π interaction) contribute to the stability of the SAM. This organic moiety that connects the head and end groups can be aliphatic or aromatic. The end-group is useful to functionalize the surface and confers specific properties to the surface. SAMs on Au(111) with various functional groups such as CF₃, NO₂, -OH, COOH, -NH₂, -SH, and -CN have been studied. A
small change in the end group can endow a significant change in the physical and chemical properties of the organic SAMs.\textsuperscript{40,22}

Once the molecules adsorb on the surface, they organize themselves into various ordered and closely packed arrangements. Figure 2-3 shows the orientation of adsorbed molecules in closely packed SAMs on the substrate. Three angles are used to describe the orientation of adsorbed molecule in standing up configurations. The tilt angle ($\alpha$) is the angle between the molecular backbone and the surface normal. The twist angle ($\beta$) tells about the C-C-C plane rotation with respect to the molecular axes. The azimuthal angle ($\chi$) is the angle between the projection of the molecule on the surface and the next-neighboring molecule.\textsuperscript{41} The molecular orientation of adsorbed molecules may vary depending on the substrate, the molecular backbone and the deposition conditions. As illustrated in Figure 2-3b the tilt angle ($\alpha$) can be either positive or negative and the twist angle ($\beta$) can have values ranging from 0° to 90°. For example, the largest tilt angles $\alpha$ (near 30°) have been reported for gold, whereas for the same molecules with highly oriented structures the observed tilt angle is close to 10° on silver and a 0° on mercury.\textsuperscript{22}
Figure 2-3. a) Scheme of an adsorbed alkanethiol molecule on Au(111) in close-packed structure. b) Schematic diagram illustrating the view of an all-trans conformer of individual alkanethiol molecule on a surface. (Adapted with permission from reference 12).

2.4-2 The Growth of SAM on Gold

Organosulfur molecules adsorb on gold surfaces with two different methods: 1) Solution-phase and 2) Gas-phase. The mechanism of reaction and the kinetics of SAMs of organosulfur compounds on gold in gas and solution have been extensively studied by multiple research groups and they all have shown that SAM growth on surface is a multi-step process. The transport of the adsorbate to the solid substrate began with the physisorption of molecules followed by chemisorption of the head group onto a substrate and formation of Au-S bond. Chemisorption is an exothermic process, which involves a chemical reaction between the surface and the adsorbate. These bonds form monolayers that are significantly more stable than the physisorbed bonds of LB films.
2.4-2a Solution-phase monolayer formation

Growth in solution is the popular way for the preparation of SAMs that draw attention owing to its simplicity and ability to produce well-ordered films. This simple method is based on immersion of a fresh, clean substrate into a dilute solution. One of the first examples of self-assembly from organic solution on flat surfaces came from the work of Sagiv, who studied the adsorption of mixed monolayers on surfaces of oxidized polyethylene, evaporated aluminum and smooth glass. In this process, several experimental parameters affect the structure of the SAM, for example the type of solvent, and the purity of the solution. Although, SAMs prepared from solution use to be more popular method so far, but this method has also some drawbacks. The limited information obtained during the growth process is one of the serious problems with this method. So, the gas phase method is much more applicable for in-situ monitoring of the growth mechanism.

2.4-2b Gas-phase monolayer formation

Deposition from the gas phase in UHV is the second commonly used method for the preparation of SAMs. Gas phase deposition is typically performed inside a UHV chamber that allows for an actual control of the cleanliness of the substrate. After preparing the substrate, the precursor compound with a sufficient vapor pressure, is placed to the sample chamber. One of the main limitation of vapor deposition is that the adsorbate should be volatile with an adequate vapor pressure and only a limited number of precursors fulfill these criteria. On the other hand, the absence of a solvent in this method makes the process more straightforward and desirable to study the early stages of growth and kinetics of SAM formation.
2.4-3 Mechanism of Formation of Organosulfur SAMs on Au

Previous studies on SAMs, focused mostly on the mechanism of monolayer prepared using organosulfur compounds as precursors from solution or gas phase onto flat metal substrates. These studies used mostly organosulfur compounds such as thiols (R-H) disulfides (RSSR), organic thiosulfates (RSSO₃M), and most recently alternative precursors including protected thiols/thioacetates (RSAC), organic sulfonyl chlorides (RSCl) and organic thiocyanates (RSCN) (where R is either an aliphatic or aromatic group). Identifying the exact mechanism for the formation of aliphatic, and aromatic SAMs on gold can be very challenging. The most accepted mechanism so far has been proposed is the formation of thiolate (R-S⁻) species. For example, in the case of thiols, the reaction is an “oxidative addition of the S-H bond to the gold surface, which is followed by a reductive elimination of the hydrogen”.\(^5\)

\[
\text{RS} - \text{H} + \text{Au}_n \rightarrow \text{RS}^-\text{Au}^+.\text{Au}_{n-1} + \frac{1}{2}\text{H}_2
\]

The outcome of the hydrogen atom after adsorption of the S-H group was debated for a longtime before because of the failure of surface characterization techniques to monitor hydrogen upon thiol SAM formation.\(^5\) Upon cleavage of S-H bond, the hydrogen atom released as H₂ or get adsorbed to the metal surface. Alternatively, it has also been suggested that the thiol could be adsorbed as an intact molecule.\(^5\) The most widely accepted hypothesis however is that thiol adsorption followed by dissociation of S-H bond and generation of H₂, as shown in Equation 2-1. This was supported by studies including Raman investigations of alkanethiol SAMs on smooth gold and silver.\(^5\) These studies demonstrated the lack of the S-H bands in SAMs while the spectra of neat alkanethiols, show the very intense ν(S-H) bands. These series of experiments provide the direct evidence for the cleavage of S-H bond.\(^5\) Kankate and
coworkers also presented a comparative XPS study of vapor deposited SAMs of 4-nitrophenyl thiol and bis-(4,4’-nitrophenyl)-disulfide on gold surfaces, which clearly demonstrated the elimination of the hydrogen atom during the SAM formation.\textsuperscript{36,51-67}

In the case of disulfide SAMs, the mechanism of SAM’s formation suggested to be an oxidative addition of the S-S bond to the gold surface (Equation 2-2).

\[
\frac{1}{2} RS - SR + Au_n \rightarrow RS^-Au^+.Au_{n-1} \quad 2 - 2
\]

Several studies have found that the monolayers originating from either a thiol or a disulfide species on gold surfaces have similar characteristics, and that disulfides bind as thiolates via the cleavage of the S-S bond.\textsuperscript{36,57,60,61,62,63}

Organic thiosulfates (Bunte salts) have been used as precursors to form SAMs on gold surfaces.\textsuperscript{64} The proposed mechanism is dissociation of S-SO\textsubscript{3} bond upon adsorption, followed by chemisorption of the molecules on the gold. Equation (2-3) shows the reported mechanism for the formation of the thiolate SAM from thiosulfates.

\[
RS - SO_{3}M + Au_n \rightarrow RS^-Au^+Au_{n-1} + [SO_3M]^- \quad 2 - 3
\]

(R is either an aliphatic or aromatic moiety and M a monovalent cation.)

Protected thiols/thioacetates, organic thiocyanates and sulfenyl chlorides are also used as alternatives to thiols. Thioacetates can be deprotected using acid or base catalyzed hydrolysis to form SAMs similar to thiols but the deprotection process introduces extra chemicals (reagents used for deprotection and the byproducts that subsequently formed) that affect SAM formation (Equation 2-4).\textsuperscript{65,66}
SAMs prepared using organic thiocyanates were of lower quality than those resulting from thiols. This was attributed to the strength of S-CN bond (~100 kcal/mol for p-substituted phenyl thiocyanate).\textsuperscript{31,32}

\[
\text{RS} - \text{CN} + \text{Au} \rightarrow \text{R} - \text{S}^\text{–} \text{Au}^\text{+} \cdot \text{Au}_{(n-\frac{3}{2})} + \frac{1}{2} [\text{Au(CN)}_2]^\text{–}
\]

Organic sulfenyl chlorides (structurally similar to thiocyanates) were also introduced as SAM precursors by the Houmam group.\textsuperscript{2,67} Long-range well-ordered SAMs were obtained on Au(111) using 4-nitrophenyl sulfenyl chloride as a precursor. The ability of sulfenyl chlorides to form very good SAMs was attributed to the weaker S-Cl chemical bond compared to the corresponding thiocyanates (S-CN bond). An adsorption mechanism involving physisorption of the precursor molecules on the Au surface with an electron transfer from the Au surface to the precursor molecule was proposed. The cleavage of the S-Cl bond and formation of the Au-thiolate bond along with the ejection of the Cl\textsuperscript{–} ion was supported by XPS studies.\textsuperscript{2}

In summary, it is mostly accepted that the mechanism of SAM formation on Au using organosulfur compounds involves the formation of a Au-thiolate bond. The quality of the SAM depends on several factors including the molecular backbone (aliphatic, aromatic or hybrid), the end group (small, bulky, electron donating, electroactive, electron withdrawing etc.), the strength of the S-Y bond (Y = leaving group, e.g. H, S-R, C-R, SO3M, CN etc.), the experimental conditions and the purity of the precursors.
2.4-4 Experimental Factors Influencing the Formation of Thiolate SAMs

Various factors are known to affect the final structure and the rate of the SAM formation including the solvent, the concentration and purity of the precursor, the temperature, the immersion time, oxygen concentration, cleanness of the substrate, and the structure of the precursor (chain length and terminal groups). This section discusses these factors.

1) Solvents

The solvent effect on the mechanism and kinetics of the adsorption of organic molecules on solid surfaces is not completely understood. The choice of a proper solvent for self-assembly is therefore crucial. In certain cases, SAMs of alkanethiols formed in non-polar organic solvents are less organized, while those formed from polar organic solvents are densely packed with fewer defects. Lee et al. investigated octanethiol SAMs prepared in two different solvents using STM. They obtained a well-ordered and closely packed structure in ethanol, and a less dense striped phase in toluene. Mamun et al. also used STM and XPS, to study the effect of solvent on octanethiol SAMs obtained in different solvents including ethanol, DMF, toluene, and hexane. They showed that solvents with high polarity can improve the quality of SAMs, while those with low polarity solvents have opposite effect on the SAMs quality. In general, ethanol is the most frequently used solvent for SAM preparation mostly due to its availability, high purity, low toxicity, low cost and the ability to dissolve a variety of organosulfur compounds. Other solvents like methanol, acetonitrile, dimethylformamide, tetrahydrofuran, and toluene have been successfully used for SAM formation, particularly when the precursors are not completely soluble in ethanol.
2) Temperature

The effect of temperature on adsorption and desorption of molecules on and from solid surfaces is well established.\textsuperscript{70,71} Even though the temperatures over 25 °C can accelerate the formation of SAM, it can simultaneously increase the desorption of contaminants. Chain reorganization and lateral rearrangement of adsorbates have also been observed with increasing the temperature.\textsuperscript{72} Uosaki \textit{et al.} suggested that the influence of the temperature is more prominent in the first step of the adsorption. They also showed that higher temperatures result in larger areas of the well-ordered domains with the $(\sqrt{3} \times \sqrt{3})$ R30° structure.\textsuperscript{71} STM was used to study the adsorption of benzenethiol (BT) in ethanolic solution on Au(111) up to 50 °C. It provided evidence for the formation of well-ordered and larger domains at higher temperatures compared to room temperature.\textsuperscript{73} Thermal annealing is also suggested to induce structural changes due to the lateral movement of molecules on the surface. It affects the size of the domains and also helps reduce the surface defects.\textsuperscript{74,75,76,77} Although the structure and kinetics of SAMs formation may be improved by increasing the temperature but an accurate control of the temperature is necessary to avoid competitive desorption of a number of adsorbed molecules during the modification process.\textsuperscript{78}

3) Concentration and Immersion Time

Concentration and immersion time are inversely related parameters. At higher concentration of thiols, a shorter immersion time is required to form a complete monolayer because the thiol adsorption is limited by mass transport. Typically, high quality SAMs can be obtained by using μM to mM adsorbate concentrations and adsorption times from a few hours to a few days. The minimum concentration required for the formation of a dense SAM is 1μM. Concentrations below this number combined with short modification times (seconds) lead to
formation of low coverage SAMs. Longer immersion times are required for the reorganization and ordering of the adsorbates, and for the decrease (or elimination) of pinholes and conformational defects especially for alkylthiols. Typically, a modification time of 12-18 h is required. It may however take several days to achieve a highly reproducible SAM in certain cases.\textsuperscript{13}

4) Effect of Oxygen in Solution

Very little is known about the effect of oxygen on the rate and structure of SAMs. Previous studies demonstrated that preparing SAM with degassed solvent and under an inert gas, such as nitrogen or argon, before and during the process significantly improves the reproducibility. It has been speculated that minimizing the oxygen content in the solution limits the rate of oxidation of thiols to other oxygenated species. This phenomenon is more prominent in SAMs prepared on silver or copper compared to gold.\textsuperscript{21,22}

2.4-5 The Au(111) Surface

Gold is one of the most popular metal substrates for the formation of the self-assembly of organic molecules. Gold is a unique element with a face-centered cubic structure that its (111) face reconstructs.\textsuperscript{79} This type of reconstruction has not been observed for other (111) surfaces such as Pd, Cu and Ag.\textsuperscript{80} This reconstruction, known as a herringbone reconstruction, reduces the energy of the surface and is critical to the adsorption process.\textsuperscript{79-81}

A typical STM image of a reconstructed Au(111) surface exhibiting the characteristic herringbone reconstruction is shown in Figure 2-4. This reconstruction has a \((22 \times \sqrt{3})\) unit cell in which 23 atoms of the top layer are placed on top of 22 atoms of the second layer. This compression causes an extra 4.4\% Au atoms in the surface of gold.
2.4-6 Low and High Coverage Structures of Organosulfur SAMs on Au(111)

2.4-6a Low Coverage Phase

Alkanethiols SAMs on gold, with low coverage have been widely investigated. They give rise to striped phases where the adsorbed molecules are laying down on the surface or having larger tilt angles. These structures have generally been described by \((p \times \sqrt{3})\) unit cells where \(p\) is an integer usually in the order of once or twice the fully extended thiolate length for a head to head/head to tail configuration. The value of \(p\) changes in the range of \((0.84 \pm 0.04)\) Å per methylene group. Various striped phases have been reported in the literature. They have a different long dimension \(p\) and the same short dimension, equal to \(\sqrt{3}a\), where “\(a\)” is the
Au lattice constant. Increasing the dose/concentration of the precursor or the incubation time initiate a phase transition from the laying down structures to packed phases with less tilted molecules.

2.4-6b High-Coverage Phase

In the high-coverage phase, molecules form the highest possible packing arrangement to reach the saturation coverage. Many experimental techniques such as X-ray, FTIR, AFM and in particular STM showed that this saturated phase corresponds to a \( (\sqrt{3} \times \sqrt{3}) \) R30° structure with respect to the Au(111) surface. The sulfur atoms are arranged in a hexagonal shape where the thiol–thiol nearest neighbor distance is \( \sim 5 \) Å. This surface structure strongly suggest a surface coverage \( \Theta = 1/3 \) with a tilt angle of \( \sim 30^\circ \).\(^{85}\)

The \( (\sqrt{3} \times \sqrt{3}) \) R30° structure is the simplest structure observed for high coverage SAMs. Other \( c(4\sqrt{3} \times 2\sqrt{3}) \) superstructures have also been reported and are referred to as \( c(4 \times 2) \) phases. These superstructures contain four molecules per unit cell with at least two different adsorption geometries. Figure 2-5 shows the proposed structural models for the \( (\sqrt{3} \times \sqrt{3}) \) R30° structure as well as the \( c(4\sqrt{3} \times 2\sqrt{3}) \) superstructures on the Au(111) surface. The \( (\sqrt{3} \times \sqrt{3}) \) R30° structure is composed of molecules with similar adsorption site and arrangement, whereas the \( c(4 \times 2) \) phases are composed of differently absorbed molecules. The various colors in the reported models (Figure 2-5e-f) correspond to these differently adsorbed molecules and STM images show indeed different degrees of brightness.\(^{85,86}\)
2.4-7 Dynamics

Evolution of surface structures doesn't stop after the SAM formation. It was shown that adsorbed species on the surface are not static but rather highly dynamic.\textsuperscript{94,95} Structural transformations in SAMs were directly observed in real time imaging using STM and AFM. Using sequential high-resolution STM imaging in air of alkanethiolate SAMs, Teran Arce \textit{et al.} showed fluctuations between the $(\sqrt{3} \times \sqrt{3}) R30^\circ$ and c(4$\sqrt{3}$ x 2$\sqrt{3}$) phases.\textsuperscript{96} The reversibility of the structural fluctuations prompted the authors to suggest that both lattices had similar energy. DFT calculations confirmed that the energy difference of these two structures is very small.\textsuperscript{57} Potential dependent transformations of surface structures in electrolyte solutions have also been reported.\textsuperscript{97}
2.4-8 Characterization of Defects on SAMs

Despite the general high degree of structural order observed in SAMs, defects are also usually present. Various factors have been shown to affect the presence and amount of structural defects including the cleanliness of the substrate and the purity of the incubation solution and precursor. Defects have also been shown to result simply from intrinsic factors as SAMs are dynamic systems with complex phase behaviors.13 Typical defects include missing rows, particularly in short alkanethiols SAMs (Figure 2-6a), vacancy islands (Figure 2-6b), molecular defects, where molecules are disordered or absent (Figure 2-6d), and domain boundaries, where molecules exhibit high degree of disorder (Figure 2-6c). Molecular defects are either in the form of vacancies known as pinhole defects or regions where the hydrocarbon chains have a certain degree of disorder. These types of defects are present even in well-ordered, alkanethiolate SAMs.87

STM and AFM images of well-ordered SAMs on Au both from solution and gas phase have revealed 2D gold vacancy islands or etch pits.98 Poirier et al. suggested that the adsorption of alkanethiol molecules results in the removal of extra gold atoms from the surface due to the weakening of the Au-Au bond, leading to these etch pits. They explained that the (22 x √3) herringbone structure of the clean Au(111) surface is lifted by the adsorption of alkanethiol molecules. This process is followed by the relaxation of surface atoms and the formation of adatoms on, and vacancies in, the surface layer.98,99 It has been studied that the density of etch pits decrease with decreasing the concentration, and increase with decreasing the length of the hydrocarbon chain.87
Figure 2-6. Schematic representation of possible SAM defects. a) Missing row. b) Vacancy islands. c) Domain boundaries. d) Molecular defects.

2.4-9 Aromatic Organosulfur SAMs on Au

While alkylthiolate SAMs have been widely studied, aromatic SAMs are attracting increasing attention due to particular characteristics and potential application in molecular electronics devices. The presence of delocalized π-electrons in aromatic rings is behind the particular conductivity of aromatic SAMs. The rigidity of phenyl rings also reduces their molecular flexibility and affects the SAMs structure and reactivity. The lateral intermolecular interactions of aromatic structure are stronger than those of aliphatic ones and can lead to different structure. STM studies demonstrated that the π–π stacking of aromatic molecules has a tendency to arrange the molecules into polymer-like chains.\cite{101,102} Modifying the surface properties of aromatic can be readily achieved by introducing various functional groups on the phenyl ring. It is also expected, due to the stronger π–π interaction and rigidity of the backbone, that a change of the substituent on the phenyl ring (at the para position) will alter aromatic SAMs
Benzene thiolate SAMs with various densities and tilt angles have been obtained. While molecular dynamics calculations and a few experimental studies have suggested that long range ordered (√3 × √3) and (4 x 2) structures of BT SAMs on Au(111) phases are unlikely to form, other studies have shown that these structures can indeed be obtained, although not as easily as with aliphatic thiols. Vacancy islands have also been reported to be more scattered in number and density with aromatic thiols while small adatom islands are more abundant. It was also shown that Au adatoms and vacancies have less mobility in aromatic SAMs (Figure 2-7).

![Proposed models for the formation of vacancy islands and adatom in (up) aliphatic and (down) aromatic SAMs on Au(111).](Adapted from reference 98)

The common limitation for practical applications of aromatic SAMs is related to the higher degree of defects usually explained by the relatively bulky and non-spherical shape of the phenyl ring. Several strategies have been used to mitigate this problem. These include using hybrid aliphatic-aromatic molecules by adding an alkyl spacer group between the sulfur...
head group and the phenyl group, increasing the number of aromatic rings and annealing, and increasing the solution temperature to 50 °C. While the introduction of insulating alkyl spacers has been shown to improve the structure of SAMs resulting in long range ordering, this was at the expense of the desirable conductivity which is diminished. Increasing the number of aromatic rings can lead to higher conductivity but also drastically lowers the solubility of the precursors.

2.4-10 STM Imaging of Organosulfur SAMs

STM is a very important technique for the analysis of the physical structure and electronic properties of SAMs. While it has provided a huge amount of information on conducting surfaces in general and organic thin films in particular, certain aspects are still not totally understood. STM detects the local density of states (LDOS) near the Fermi level of energy and the obtained images show in general a combination of bright and dark spots. The nature and origin of the contrast variations observed in the STM images are poorly understood. They have been associated respectively to the terminal group, the molecular backbone, or the S atom of the adsorbed molecule.

The first high resolution STM images of thiol based SAMs on Au(111) were reported by Widrig et al. Because they were able to image modified and non-modified gold surfaces under the similar tunneling currents and voltage conditions, they suggested that, during imaging, the tip is positioned close to Au-S interface. They therefore concluded that in the obtained STM images, the bright spots result from tunneling current that flows between the tip and the sulfur atom bound to Au. Later studies showed however that this imaging mechanism cannot explain the modulation in brightness in the c(4 x 2) lattices. Theoretical calculations and experimental results suggested that the tip probes either the hydrocarbon chains or the terminal groups,
proving hence a better explanation for the brightness modulation in the c(4 x 2) lattice. Further theoretical calculations performed by Zeng\textsuperscript{1} and Li et al\textsuperscript{121} also suggested that the STM is able to probe the hydrocarbon chain despite the large HOMO-LUMO gaps in the alkanethiol SAMs. They explained that the electronic structure of an absorbed molecule on Au(111) surface is different than that of the free molecule. Chemisorption process results in emergence of new electronic states in the energy gap of the alkanethiol. They concluded that STM basically images those states that are localized at the tail carbon–hydrogen groups which reflect the terminal groups in the SAM.

The Houmam group reported the ability of the STM to provide insight on the terminal group in standing up SAMs. In this study high resolution images of 4-nitrophenyl sulfenyl chloride SAMs on Au(111) provided sub-molecular details of the terminal group. A bright spot was observed for each oxygen atom of the nitro group. This work indeed stirred up one of the heavily debated questions concerning the ability of the STM to provide sub-molecular structural information for standing-up SAMs in air at room temperature.\textsuperscript{122}

While experimental studies highlighted the involvement of topographic effect in the STM images, recent DFT studies propose that, even though the physical structure may explain the STM contrast of alkanethiol SAMs, the influence of LDOS cannot be ruled out.\textsuperscript{85,121}

Utilization of constant current mode of STM to investigate annealed undecanethiol SAMs under UHV. STM images revealed two distinct c(4 x 2) structures with the STM contrasts that remained highly reproducible and reversible upon modulation of the imaging conditions. They concluded that these contrast transitions likely indicate probing of the corresponding LDOS during modulation of the tunneling conditions, as opposed to reorientation of the molecules.\textsuperscript{85}
The interpretation of STM images can be challenging and caution should be exercised during the data acquisition and explanation of STM images taken from organosulfur SAMs on Au(111). The effect of the tunneling conditions (i.e. the bias voltage, the tunneling current, the distance between tip and sample), the nature and the length of the molecular backbone (aliphatic or aromatic, long or short chains), and the odd or even number of carbon atoms on the aliphatic chain can influence the STM images and consequently the interpretation might differ. In addition, the binding sites on the Au surface, the hybridization of the sulfur head group, the mobility of the molecules on the surface, the changes induced by the STM tip (SAM perturbation, alteration of the adsorption sites or the molecular conformation etc.) and the changes associated with the substrate surface (surface reconstruction or stress) can also interfere with the molecular orientation of the SAM.
Chapter 3. Materials and Experimental Techniques

3.1 Chemicals

4-Nitrothiophenol (≥98% from Santa Cruz Biotechnology, Inc), 4-Nitrophenyl disulfide (99% from Aldrich), N,N-dimethyl formamide (DMF, Fisher Scientific), anhydrous ethanol (EtOH, absolute from Commercial Alcohols), potassium hydroxide (KOH, 99.99% semiconductor grade from Sigma Aldrich) and sodium hydroxide (NaOH, 99.99% semiconductor grade from Sigma Aldrich) are used without further purification. A gold wire (0.76 mm diameter, 99.999% from Alfa Aesar) and freshly cleaved mica sheets (V1 Grade, Ted Pella) are used to deposit thin films of Au (111). Chromo-sulfuric acid (2 mL of chromium trioxide, Cr₂O₃ from Chromerge ®, Bel-Art, and 200 mL of sulfuric acid, H₂SO₄, 95-97%, semiconductor grade from Riedel-de Haën) is used to clean Au (111) substrates.

3.2 Glassware

All glassware for the experiments were pre-cleaned in a KOH/H₂O/ETOH bath and then in a H₂O/HCl bath. All glassware then rinsed thoroughly with deionized water followed by Milli-Q water. The equipment was subsequently stored in an oven.

3.3 Experimental Techniques

A number of analytical techniques were used in this work to characterize the modified gold surfaces including CV, STM, XPS and PM-IRRAS. CV was employed to evaluate the reductive/oxidative desorption of absorbents and determine the surface coverage of SAM. This was achieved by electrochemical stripping of adsorbed species on polycrystalline solid gold electrodes. STM was used to image the modified surfaces and provide detailed information about the formed structures, phases, defects, etc. XPS was used to analyze the elemental composition,
the chemical state of each element and any contaminant present on the modified gold surface. PM-IRRAS was used to probe functional groups of the adsorbed organic molecules. The relative peak ratios were used to determine the tilt of the adsorbates.

3.3-1 Cyclic Voltammetry

Cyclic voltammetry (CV) is a simple, powerful, and rapid electrochemical technique used for quantitative and qualitative measurements of the electrochemical properties of electroactive species (i.e. a species that can be oxidized and/or reduced). This technique is very useful in obtaining information about mechanistic, kinetic and thermodynamic data of electroactive species both in solution and on surfaces (adsorbates). A standard CV experiment employs a cell composed of three electrodes: a working electrode, a counter electrode, and a reference electrode. The principal of this technique is based on modulating the applied potential at the working electrode in both forward and reverse directions while monitoring the current at the same electrode. The potential of the working electrode is swept linearly with time at a fixed rate from an initial potential (E1) where no redox reactions occurs to a switching potential (Es) and then reversed to the initial potential. This process can be reversed several times in both directions as illustrated in Figure 3-1.
Figure 3-1. Potential – time excitation signal in cyclic voltammetry experiment.

The readout of the experiment will be presented as an I-E curve, called cyclic voltammogram (Figure 3-2). By convention, a positive current reflects an oxidation, whereas a negative current represents a reduction. For example, for a reversible CV, in a forward scan, the electrode will act as a cathode (reduction) and in a reverse scan it will act as an anode (oxidation). An irreversible cyclic voltammogram can also be observed if relatively fast chemical reactions follow the initial electron transfer.
In this study cyclic voltammetry is used to evaluate the reductive desorption of organosulfur monolayers adsorbed on polycrystalline solid gold electrodes. Previous studies have suggested that alkanethiols and alkyl disulfides form similar Au-alkylthiolate monolayers on gold (Figure 3-3). Reductive desorption has been extensively used to evaluate a wide range of thiolate SAMs. There is also a general agreement on the mechanism of the reductive desorption of organosulfur monolayers which is described to involve one electron per molecule (Equation 3-1).

$$\text{Au} - \text{SR} + e^- \rightarrow \text{Au}^0 + \text{RS}^-$$

Previous studies on alkanethiol SAMs on polycrystalline gold electrodes have shown that sufficiently negative potentials cause the desorption of alkanethiol monolayers in acidic, neutral, and basic solutions. The desorbed thiolate can also oxidatively reabsorb on the surface if the potential is scanned back in the positive direction and if the thiolate species does not diffuse
away from the electrode surface and remains on and/or near the electrode surface. This can be observed as a small anodic peak in the CV.

In reductive stripping voltammetry, the shape, the area, and the position of the reductive desorption peak provide practical knowledge about the SAM such as the coverage, stability and orientation of adsorbates.\textsuperscript{126-131}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3-3.png}
\caption{Thiolate SAM formation from thiols and disulfides.}
\end{figure}

For this thesis, Autolab PGSTAT30 (EcoChemie) system was used for all electrochemical measurements and downstream analysis. A three-electrode type glass cell, kept at 25 °C and under a nitrogen flow, was used for all CV experiments. The working electrode is a solid polycrystalline gold electrode (2 mm diameter). The counter and reference electrodes are a saturated calomel electrode (SCE) and a platinum wire, respectively. All electrodes were carefully polished and thoroughly cleaned by ultrasonic rinsing with ethanol. Polycrystalline solid gold electrodes were additionally cleaned by electrochemical cycling in a 0.5 M KOH aqueous solution.
3.3-2 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was developed in 1960 by Kai Siegbahn at the university of Uppsala, Sweden and was awarded the Nobel Prize in physics in 1981 for developing this powerful analytical technique. This method was initially called “electron spectroscopy for chemical analysis” (ESCA) because it provides information about the chemical state rather than only elemental composition of surface. It is a sensitive technique to interrogate the surface for all elements with an atomic number \( Z \geq 3 \).

The underlying principal of this technique goes back to 1887, when Heinrich Hertz first described the photoelectric effect and then later on followed by Albert Einstein in 1905 who explained this effect with a simple yet important mathematical description (Equation 3-2).\(^{134,135}\)

\[
E_k = h\nu - E_B
\]

Where \( h \) is Planck’s constant, \( \nu \) is the frequency of the incident photons, \( E_k \) and \( E_B \) are the kinetic energy and binding energy of the photoelectron, respectively.

XPS, requires a high vacuum or ultra-high vacuum environment and is based on the photoelectric effect principal. XPS involves the irradiation of the sample surface inside the UHV with X-rays of a known energy and the subsequent analysis of the energy of the emitted photoelectrons. Normally, the sample is bombarded with a soft X-ray beam (200 - 1500 eV). The most commonly X-ray sources are AlK\( \alpha \) and MgK\( \alpha \) with a corresponding energy of 1486.6 eV and 1253.6 eV, respectively. Core electrons are inner-shell electrons that are closer to the nucleus, and therefore require more energy to expel compared to valence electrons.

Once the electrons are ejected from the sample, their number and kinetic energy are analyzed by an appropriate electron energy analyzer. Since the energy of an X-ray is known, the
binding energy of the electron \( (E_B) \) can be calculated by using Equation 3-3, where \( \Phi \) is the spectrometer work function. The \( E_B \) is unique for each element and resembles the identity of the elements present in the substrate and its environment.\textsuperscript{133,136} A schematic diagram illustrating the photoemission process is shown in Figure 3-4.

\[
E_B = h\nu - E_K - \Phi
\]  

Figure 3-4. Schematic diagram illustrating the photoemission process.

The XPS data is presented as a plot of electron count versus either the binding energy \( (E_B) \) or the kinetic energy \( (E_K) \) of the measured photo-excited electrons (Equation 3-2). The plot has characteristic peaks for each element found in the surface of the sample. The peaks in the photoelectron spectrum correspond to the electrons in different subshells of the atom (1s, 2s, 2p,
etc.). Photoelectrons that are originated from a certain orbital demonstrate a unique binding energy so the identity of the element present on the surface can be revealed by looking at the plotted spectrum and the designated value of the peak energy.\textsuperscript{137,138}

The XPS instrument consists of an X-ray source, an electron collection lens, an electron energy analyzer and an electron detector, all placed within an ultrahigh vacuum (UHV) chamber (Figure 3-5).\textsuperscript{139} In order to achieve an ultra-high vacuum environment, the system utilizes a special pump system. The ultra-high vacuum environment prevents from contamination of the surface.

Essentially a focused beam of X-ray illuminates an area of a sample causing electrons with a range of energies and directions to eject. Obviously, the X-ray beams should provide energy to overcome the binding energies of the core electrons. Ejected electrons pass through a set of electrostatic/magnetic lens units that collect a proportion of these ejected electrons and transferred them onto the analyzer entrance slit to be sorted according to their energies.\textsuperscript{140}

The X-ray source is mostly a twin anode that generates a broad X-ray beam of Al K$\alpha$ ($h\nu = 1486.6$ eV) or Mg K$\alpha$ ($h\nu = 1253.6$ eV). The direct X-ray sources deliver high intensity photons bombarding the sample surface, that in return led to the high flux of photoelectrons to the detector, which causes a wide X-ray line width, satellite X-ray peaks that may cause sample damage. Collectively these factors can affect the quality of the XPS spectrum. To reduce the adverse effect of direct X-ray radiation, monochromators are installed inside the XPS systems. Monochromators are typically made of silicon, quartz and germanium crystals, that increase the signal to background ratio by selecting emission lines, removing the Bremsstrahlung continuum and consequently minimizing sample damage from heat and unwanted radiation.\textsuperscript{138} For example, The AlK$\alpha$ source has a photon energy of 1486.6 eV with a full line width at half maximum of 0.9
The quartz crystal monochromator used with this source narrows the line width to 0.25 eV resulting in a greater resolution for distinguishing different chemical species.\textsuperscript{133,138,142}

\textbf{Figure 3-5.} Basic components of a monochromatic XPS system.

In this study, XPS was only used to identify chemical species present on the surface. All experiments have been conducted in a commercial ultrahigh vacuum (UHV) system (Omicron) with a base pressure of $5 \times 10^{-11}$ Torr. An Al K\textalpha\ source (1486.6 eV) was used to generate X-ray. The system consists of a hemispherical sector analyzer (operates at a pass energy of 20 eV) which is paired to a multichannel electron detector. All XPS spectra for the modified gold presented in this thesis are referenced against Au 4f\textsubscript{7/2} peak at 84.0 eV with takeoff angle of 75°. Deconvolution of the XPS peaks was done using origin 7.0 SR0 v7.0220 software.
3.3-3 Polarization Modulation Infrared Reflection Absorption Spectroscopy

3.3-3a Infrared Spectroscopy

Infrared (IR) spectroscopy is a broadly used spectroscopic technique due to its ability to provide information about the structure and in particular functional groups of molecules. The absorption of IR radiation by a molecule brings a change in the vibrational and rotational modes of chemical bonds.\textsuperscript{143} IR spectroscopy follows a selection rule, where only vibrational/rotational transitions associated with a change in the dipole moment give rise to a peak in the IR spectrum.\textsuperscript{144,145}

Early IR instruments were called dispersive because they simply used prisms and grating monochromators in order to collect the absorption spectrum. These early instruments had a slow scanning process. Modern IR instruments, called Fourier transform infrared (FTIR) instruments, use Fourier transform method to rapidly scan samples by continuously monitoring all frequencies and transform the signal into a frequency spectrum. This technique is a simple, rapid, less expensive and highly sensitive technique to obtain structural information of organic and inorganic samples even at the interface (e.g. gas/solid, liquid/solid and gas/liquid).\textsuperscript{146}

Until the 1960s, the first generation of IR spectrometers were not able to obtain useful IR spectra of thin films on metal surfaces (a few nanometers) due to poor signal to noise ratios, as the amount of absorption is proportional to the path length. In 1966, Greenler \textit{et al.} used the reflection method to study the IR spectrum of thin films on metal surfaces. They discovered that using IR polarized radiation parallel to the plane of incidence at near grazing incidence could increase the IR absorption up to 5000 times which subsequently allows the measurement of film thickness at the Å level.\textsuperscript{147} Longer time accumulation may be required due to the very small
absorption peak obtained by infrared reflection–absorption spectroscopy (IRRAS). In order to accurately remove the background signal, both reference and sample substrates need to be measured. The absorption of H\textsubscript{2}O and CO\textsubscript{2} can significantly affect spectrum. In the late 1970s, PM-IRRAS was developed to alleviate some of the difficulties of the IRRAS setup. This improvement is mainly achieved by modulating the polarization of the incident IR radiation that eliminates the absorption of CO\textsubscript{2} and H\textsubscript{2}O from the sample environment. PM-IRRAS is a very powerful alternative for the characterization of thin films, monolayers or sub-monolayers on metals. The technique also provides information about the nature and the orientation of the adsorbed species with higher sensitivity.\textsuperscript{148,149}

3.3-3b Principals of PM-IRRAS

In order to remove the background signal from the experimental film, the IR beam must be linearly polarized as a first step. This can be achieved by passing the radiation through a polarizer grid. The two linear polarization states are referred to as p- and s-polarization. These polarizations are most important for reflection and transmission. The p-polarized light has an electric field parallel to the plane of incidence while the s-polarized light has electric field vectors perpendicular to the plane of incidence. The PM-IRRAS technique measures the surface specific FT-IR spectra of materials by calculating the differences in the reflection of s- and p-polarized light from interfaces.

Upon incidence of the polarized light on the surface, the light is partially reflected and partially transmitted into the second medium. The intersection plane between the incident and the reflected beams is called plane of incidence. In the event that the incident beam is split into p- and s- polarizations, they each correspond to differentially directed electric fields. If the value of the incident beam angle is larger than the critical angle, the entire beam reflects off the interface
and no light is transmitted into the second medium. At the point of incidence, the electric field vector of s-polarized radiation (I_s) of the incident and reflected waves are oriented in opposite directions because the s-polarized radiation undergoes a phase shift of $180^\circ$. As a result, the electric field of the s-polarized frequencies becomes zero (i.e. $E_s = 0$) at the metal surface, which is demonstrated in Figure 3-6. This prevents absorption of the incident IR radiation by any chemical species that is absorbed at (or in close proximity to) the electrode’s surface. Therefore, the s-polarized radiation is exclusively sensitive to the molecules present in the bulk of the solution and not on the surface of the electrode. Conversely, the electric field vector of the p-polarized radiation is subjected to a very small shift, given that the angle of incidence is less than $80.7^\circ$. The cumulative electric fields of the incident ($E_{pi}$) and reflected ($E_{pr}$) of the p-polarized waves at the point of reflection demonstrate an electric field enhancement in the direction normal to the surface, as depicted in Figure 3-6. The p-polarized spectrum contains information about the species located at the metal surface and in the bulk of the solution.
Figure 3-6. Illustration of the phase shift of the electric field vector for a) s-polarized and b) p-polarized radiation upon reflection at an air/Au interface.

These enhancement and cancellation of the electric field vectors for the p- and s-polarizations at the metal surface are described based on the surface selection rules. The absorption of IR radiation by molecules on the surface will change the dipole and consequently induce an image dipole into the metal. If the change in the dipole is parallel to the metal surface it will cancel out the IR absorption but if it is perpendicular to the metal surface it will enhance the IR absorption. In Figure 3-7 for example, based on this rule, image dipoles are cancelled out in laying down configuration and are enhanced for the upright molecules.
Figure 3-7. Schematic showing the image effect for the metal surface.

PM-IRRAS spectroscopy uses the surface selection rules to differentiate the IR spectrum of the species adsorbed at the surface from the background species in solution. Therefore, the background spectrum should be collected using s-polarized radiation prior to the p-polarized IR spectrum, containing the background and surface species. The PM-IRRAS absorption spectrum, $\Delta S$, of the adsorbed film is calculated by using the following expression:

$$\Delta S = 2 \left( \frac{I_s - I_p}{I_s + I_p} \right)$$

The resulting PM-IRRAS spectrum then corresponds to the IR spectrum of only the species adsorbed on the surface of the metal and quantitative determination of the average orientation of the molecules on the surface by quantifying the spectrum.\textsuperscript{150,151}

In this study, the IR spectra were collected on a Varian 660-IR spectrometer with a liquid nitrogen cooled high sensitivity MCT-A detector. The modified gold slide was placed on top of a Pike Technologies Advanced Grazing Angle (AGA) attachment. The infrared radiation was directed through a ZnSe static polarizer and focused onto the surface of the gold slide at an
incident angle of 80° via the AGA attachment. The s-polarized radiation was first obtained by rotating the static polarizer to 90° and collecting 512 scans at a resolution of 4 cm⁻¹. Immediately after acquiring the s-polarized single beam spectrum (I_s), the p-polarized spectrum (I_p) was obtained by rotating the static polarizer to 0° and collecting 512 scans at a 4 cm⁻¹. The s- and p-polarized single beam intensities were used to manually calculate the PM-IRRAS spectra according to the Equation 3-4:

\[ \Delta S = \frac{2(I_s - I_p)}{(I_s + I_p)} \]

Based on the surface selection rules, the spectra show only the IR absorption of species directly adsorbed to the gold surface and are free from interfering background species.
3.3-4 Scanning Tunneling Microscopy

3.3-4a Introduction

The scanning tunneling microscope (STM) was developed by Gerd Binning and Heinrich Rohrer at IBM Zürich in 1981 who shared the Nobel Prize five years later for their brilliant invention.\textsuperscript{152,153} STM is a powerful experimental technique for the investigation of surface morphology. This technique has the ability to provide 0.1 nm lateral and 0.01 nm depth resolutions.\textsuperscript{154} Figure 3-8 shows the basic components of STM that include: 1) a scanning tip 2) a piezoelectric tube 3) a distance control and scanning unit 4) a tunneling current amplifier 5) a vibration isolation system and 6) a data processing unit (computer).

The scanning tip is a simple but crucial part of the system. The tip has to be conductive and atomically sharp to pass most of the tunneling current through a single atom. Tungsten, platinum-iridium and gold tips are the most common types of tips. The tips typically are made by mechanical cutting, grinding or electrochemical etching.\textsuperscript{154} The piezoelectric scanner is commonly fabricated from lead zirconium titanate (PZT) by compacting a powder form and sintering. This material provides 3-dimensional movement for the STM tip and can expand and contract at nanoscale depending on the voltage applied. This allows for precise control of the horizontal positions $x, y$, as well as the height $z$ of the scanning tip (tip is attached to the piezo drive). Since the STM is very sensitive to vibration, an isolation system is important to reduce inner vibrations and isolate the system from external vibrations. The data processing unit (computer and software package) is the last component that records the tunneling current and controls the voltage to the piezoelectric tubes to produce a 3D map of the sample surface.\textsuperscript{155}
3.3-4b Principle of Operation

The principle of STM can be explained by the quantum mechanical tunneling effect. Essentially, small particles such as electrons behave like wave that allow them to penetrate potential barriers.\textsuperscript{156} The basic principle of electron tunneling is demonstrated in Figure 3-9. In this technique a conducting tip is brought very close to the examined surface until a narrow gap of empty space is left between them (~ 0.3 – 1 nm), called energy barrier. When no bias voltage is applied between the tip and sample, electrons are confined under their Fermi levels (E\textsubscript{F}), and the electrons cannot flow in either direction due to the equal Fermi levels of both the tip and the sample. The Fermi level can be raised by applying a voltage. When a bias is applied between the two, as shown in Figure 3-9b the tunneling waves of the sample (\psi\textsubscript{s}), and tip (\psi\textsubscript{t}) electrons,
overlap in the barrier gap, causing a tunneling current to flow through. Depending on whether the voltage is applied to the sample or tip, electrons can tunnel between the occupied and unoccupied state of the other side. This tunneling current can be measured and then converted into a topographical image of the surface.\textsuperscript{156}

The tunneling current has a very important characteristic; it has a very high sensitivity to the barrier width $z$ which is proportional to the probability of electrons across the barrier. This has been solved with solutions of Schrödinger’s Equations for electrons inside a barrier:

\[ \psi(z) = \psi (0) e^{-\kappa z} \]  \hspace{1cm} 3 - 5

where

\[ \kappa = \frac{[2m_e (V_B - E)]^{1/2}}{\hbar} \]  \hspace{1cm} 3 - 6

Where $\kappa$ is the decay constant, $V_B - E$ is the barrier potential for electrons with energy $E$, $Z$ is the barrier width, $m_e$ is the effective mass of the electron and $\hbar$ is the Planck’s constant.\textsuperscript{95} The current is exponentially proportional to the barrier width $Z$:

\[ I_t \propto e^{-2\kappa z} \]  \hspace{1cm} 3 - 7

Equation 3-6 and 3-7 cumulatively show that the tunneling current is proportional to tip-sample gap, the bias voltage and the local density of state (LDOS) of the sample, Thus a very small change in the tip-sample gap lead to large changes in the tunneling current.
3.3-4c Operation Modes of STM

1- Topographic STM Operation Modes

There are two imaging modes available in STM: 1) constant current imaging and 2) constant height imaging.\cite{157}

The constant-current mode is the most commonly used mode and produces images of the surface contour. In this mode, a feedback loop keeps the tunneling current constant. For example, when the system detects a change in tunneling current, it alters the voltage applied to the Z-axis scanner to change the gap between the tip and the sample, so the tip height continues to follow a contour of a constant density of states during scanning and provides information on the topography of the sample surface. Although this mode is time consuming, it is best used for irregular surfaces.
In constant height mode, height of the tip is kept constant over the sample surface and the tunneling current is measured. The surface image is produced using the current as a function of lateral position. This mode is best used for atomically flat surfaces since the gap between the tip and the surface is constant the tip may crash in uneven surfaces (Figure 3-10).

**Figure 3-10.** Modes of STM Operation: a) constant current and b) constant height.

2- Tunneling Spectroscopy STM Operation Modes

Tunneling current in the STM imaging mode, recorded as a function of lateral (x - y) position at a constant bias voltage. A plot of the tip height as a function of position generates the topography. But in the tunneling spectroscopy mode, the current is continuously monitored as a function of a changing bias voltage (I-V curve). Tunneling spectroscopy as a function of the bias voltage can be obtained by carefully placing a STM tip above a designated place on the sample with the height of the tip fixed. I-V curves were recorded after the feedback is turned off. The slope of the I-V curve at each measured voltage often called the dI/dV-curve which corresponds to the electron density of states at the local position of the tip, (LDOS).158
3.3-4d Calibration of STM

Highly oriented pyrolytic graphite (HOPG) is routinely used as a standard in STM calibration for high-resolution imaging. The STM image of HOPG should demonstrate normally a closely packed hexagonal array where each atom is circled by six other atoms. We measure the distance between any two atoms as 0.246 nm (Figure 3-11). In this work HOPG has been used to calibrate the STM and quality control the STM data obtained in different times.

![Figure 3-11. Constant - current STM image of HOPG a) 6 x 6 nm².](image)

In this study, STM images obtained in air with Agilen 5500 scanning probe microscope with Pico view 1.8.2 software. Tungsten wire, (0.25 mm diameter, 99.95%, Alfa Aesar) was used to prepare the probes using electrochemical etching technique in a 3 M NaOH (99.99%, Semiconductor Grade, Sigma Aldrich) aqueous solution. Images were obtained using constant current mode at scan rates ranging from 4.1 lines / second to 4.8 lines / second.
Chapter 4. 4-Nitrothiophenol and Bis (4-nitrophenyl) Disulfide as Precursors for Modification of Gold

This chapter describes the use of 4-nitrothiophenol and bis (4-nitrophenyl) disulfide to produce nitro-terminated aromatic SAMs on gold surface. The modification was done by incubation in a solution containing the precursor. Various solvents (ethanol, acetonitrile, DMF), solvent mixtures (THF:Methanol) and incubation times (from minutes to 48 hours) were used. Because our main goal was to obtain dense SAMs similar to those observed with the 4-nitrosulfenyl chloride, only results leading to the highest coverage for the two precursors are presented. Two types of gold surfaces were used, polycrystalline gold electrodes and Au(111) surfaces. The polycrystalline gold electrodes were used for the stripping cyclic voltammetry investigation and hence coverage determination, while the Au(111) were used for the XPS, PM-IRRAS and STM investigation and hence structural characterization. Since the STM study was crucial to this project, great care was given to producing Au(111) surfaces and STM tips of high top quality. These two aspects will be described first before reporting the results of the investigations of the two precursors.

4.1 Preparation of Au(111) on Mica

The most widely used methodology to prepare gold surface, is the evaporation technique where gold being deposited on a flat base to make oriented thin films. It is essential for the base to be atomically flat and for the gold particles to be able to stick to the surface. Mica is a natural silicate mineral with a layered structure and can reveal a large surface area with atomic scale flatness just by cleaving the mica sheets. In this study, Au-films were prepared by deposition of gold on a mica surface using the evaporation technique detailed bellow.
A custom-built evaporation system (MIDAS) is used to evaporate gold wires and deposit gold on a freshly cleaved mica sheet. The evaporation system consists of a bell jar (Kurt J. Lesker) and a turbo pump (Varian), that sustain a pressure of $1 \times 10^{-6}$ Torr during the procedure. A gold wire (0.762 mm diameter, 99.999%, Alfa Aesar) was heated in the evaporation chamber and deposited onto freshly cleaved mica (V1 Grade, Ted Pella). The base plate holding the mica was heated at 300 °C for 12 hours prior to the evaporation and an extra 3 hours post deposition, which improves the quality of gold surface. Samples subsequently cleaned with chromosulfuric acid, anhydrous ethanol, and Milli-Q water and dried with a nitrogen stream and stored in a desiccator until further use. The method is adapted from Derose et al.\textsuperscript{16} STM is used to assess the quality of each Au(111) substrates batch before modification. Figure 4-1 shows STM images of Au(111) obtained using this procedure.

Figure 4-1. Topographic images of thin gold films on mica prepared by MIDAS. (a) 800 x 800 nm$^2$, (b) 5 x 5 nm$^2$. Tip bias = +0.2 V, tunneling current = 0.8 nA, and scan rate 4.8 lines/s.
4.2 STM Tip Preparation

The preparation of the STM tip is an important step in STM experiments. The quality of the tip can directly influence the resolution of STM images. The STM-tip has to be very sharp with an atomically stable apex. A blunt tip can cause the electron tunneling to occur across a wider spatial range and induce unwanted noise. In this study, a common electrochemical etching technique has been used for etching the tungsten wires (0.25 mm diameter). Tungsten is a metal with high electrical conductivity that makes it ideal to be used as an STM tip. Figure 4-2 shows the basic tip preparation set up. In this set up, a Pt ring is used as a cathode and the anode is the steel rod to which tungsten wire is connected. The process of electrochemical etching involves applying a potential (2V) between the ring and the wire through a basic solution (3M NaOH). The wire is gradually etched away at the surface until it breaks in two halves. It is essential to suspend the W wire at the center of the Pt ring to produce more uniform etching.

Figure 4-2. The basic tip preparation set up.

Solid tungsten is oxidized or etched by OH\(^{-}\) and form tungstate anion (WO\(_4^{2-}\)). The oxide dissolves into the liquid. Equations 4-1 describes the etching process of a tungsten wire in a basic solution.

\[
\text{W} + 8\text{OH}^- \rightarrow \text{WO}_4^{2-} + 5\text{H}_2\text{O} + 4\text{e}^- \\
\text{W} + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{WO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- 
\]
solution. As STM tips can be damaged and oxidized easily, they should be stored in a desiccator. Light weight foam can be used to insert the back end of a tip for storage.

\[
\begin{align*}
\text{Cathode: } & \quad 6\text{H}_2\text{O} + 6e^- \rightarrow 3\text{H}_2(\text{g}) + 6\text{OH}^- \\
\text{Anode: } & \quad \text{W(s)} + 8\text{OH}^- \rightarrow \text{WO}_4^{2-} + 4\text{H}_2\text{O} + 6e^- \\
\text{Overall: } & \quad \text{W(s)} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{WO}_4^{2-} + 3\text{H}_2\text{O}
\end{align*}
\]

Characterization of the produced SAMs is performed using various techniques including CV, XPS, PM-IRRAS and STM.

### 4.3 Nitrothiophenol as a Precursor for the Modification of Gold Surfaces

Polycrystalline gold electrodes as well as monocrystalline Au(111) surfaces were modified using 4-nitrothiophenol in DMF. The modified polycrystalline gold electrodes were characterized with stripping CV which also allowed determination of the SAM coverage. The modified Au(111) surfaces were characterized using XPS, PM-IRRAS and STM.

#### 4.3-1 Stripping CV Results

Electrochemical studies are performed using a polycrystalline solid gold electrode. Electrode first physically and chemically polished and then subjected to ultra sonication in ethanol. Electrode then further cleaned electrochemically after cycling in a 0.5 M aqueous KOH solution. After cleaning, the electrode is again completely rinsed with EtOH and dried with a gentle stream of nitrogen. The pretreated clean gold electrode was immersed in a 10 mM solution of 4-nitrophenol for various length of time spanning from few minutes to 48 hours.

Figure 4-3 shows reductive stripping scans of a polycrystalline gold electrode in 0.5 M aqueous KOH after modification with 10 mM concentration of 4-nitrothiophenol in DMF at different modification times. A reductive stripping scan for the non-modified polycrystalline...
electrode is also shown for comparison. A number of interesting observations can be made from these results:

1) Figure 4-3 shows that even after a brief modification period of 5 minutes a relatively large reductive signal at -0.86 V versus SCE was detectable compared to the bare polycrystalline gold electrode in the same region. The area under the stripping peak increases with the modification time until it reaches a maximum at 5 h. For immersion times of 5 h and longer (24 and 48h) no noticeable difference was observed. These results suggest that the 4-nitrophenylthiolate adsorbs rapidly to the gold electrode and that a saturation coverage is reached within 5 h of modification.

2) The presence of a sharp peak at the 1st scan and its disappearance at the 2nd scan is suggestive of formation of monolayer on the electrode in the modification process. The monolayer then completely removed during the initial reductive scan.

3) In addition to the main reduction peak at -0.86V versus SCE, a reproducible pre-peak can also be seen. This pre-peak is usually only observed at shorter modification times. This phenomenon is likely related to a phase transition of the monolayer or a reorientation of the monolayer molecules under the influence of the applied potential.127
Figure 4-3. Time dependent cyclic voltammetry, in a 0.5 M aqueous KOH solution at 25 °C, of a 2-mm diameter solid gold electrode modified with 4-nitrothiophenol.

The area under the reductive cyclic stripping voltammetry peak and the effective area of the polycrystalline solid gold electrode were used to calculate the monolayer coverage at different modification times. Integration of the area under the reductive stripping peak at -0.86 V provides a very high charge density, higher than that expected for the reductive desorption of a thiolate monolayer. We believe that this peak is related to the complete reduction of the nitro group to the amino group (Equation 4-2) and simultaneous desorption of the monolayer as well as the contribution from the non-faradic current (Equation 4-3).

\[
\text{Au} - \text{S} - \text{ArNO}_2 + 6\text{e}^- + 4\text{H}_2\text{O} \rightarrow \text{Au} - \text{S} - \text{ArNH}_2 + 6\text{OH}^- \quad 4 - 2
\]

\[
\text{Au} - \text{S} - \text{ArNO}_2 + \text{e}^- \rightarrow \text{Au} + \text{O}_2\text{NAr} - \text{S}^- \quad 4 - 3
\]
The effective surface area of the polycrystalline solid gold electrode is calculated from the cyclic voltammetry of a 1 mM solution of ferrocene in 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆) / acetonitrile at different scan rates using Randles–Sevcik equation (equation 4-4).

\[
A_e = \frac{1}{0.4663 \times n_e \times F \times \left(\frac{nF}{RT}\right)^{\frac{1}{2}} \times D^{\frac{1}{2}} \times C} \times v^{\frac{1}{2}} \quad \text{4 - 4}
\]

Where \(A_e\) is the effective gold electrode area in cm\(^2\), \(I\) is the anodic/cathodic peak current in amps, \(n_e\) is the number of electrons transferred in the redox event (1 for ferrocene), \(F\) is Faraday’s constant in Cmol\(^{-1}\), \(R\) is the general gas constant in J K\(^{-1}\) mol\(^{-1}\), \(T\) is the temperature in K, \(D\) is the diffusion constant in cm\(^2\)/s, \(C\) is the concentration in mol.cm\(^{-3}\), and \(v\) is the scan rate in V/s.

Figure 4-4 shows a lot of the calculated coverage as a function of the modification time. The monolayer coverage increases rapidly from 5 minutes to 5h of the modification. The calculated surface coverage for a short modification time of 5 minute is 0.15ML. Further increasing the modification time, reveals a rise in coverage, plateauing at ~0.33 ML after modification for 5h. These results demonstrate the possibility of achieving very high coverage on gold using 4-nitrothiophenol.
Figure 4-4. Time dependent coverage of the monolayer deposition calculated from the reductive stripping voltammetry of previously modified polycrystalline solid gold electrodes in a 0.5 M aqueous KOH solution at 25 °C.

The stripping CV investigation showed clearly that 4-nitrothiophol can successfully be used to obtain high modification coverage similar to those obtained using 4-nitrosulfenyl chloride. Before settling with these modification conditions (10 mM in DMF for 5h or longer) various conditions (different concentrations (from 1mM to 10mM), solvents (ethanol, acetonitrile, methanol, THF) and incubation times (from minutes to 48 hours)) were tested with limited success with much lower coverages were observed. Once these modification conditions were optimized and in order to gain more insights into to the structure of the obtained SAMs, Au(111) surfaces were modified and characterized using XPS, PM-IRRAS and STM.

4.3-2 XPS Characterization

The same modification procedure for the Au(111) substrates was used for the XPS, PM-IRRAS and STM investigations. The Au(111) substrate was immersed in a 10 mM solution of
the precursor for various periods of times spanning from a few minutes to 48 hours depending on the characterization techniques intended for. Dried and degassed DMF was used as a solvent in all experiments and the modification is performed in an inert argon environment. Samples were rinsed thoroughly but gently with DMF and pure ethanol to remove physiosorbed over-layers. The samples were then dried with a gentle stream of nitrogen for 2-5 minutes.

XPS was used to determine the chemical composition of the obtained monolayers. Figure 4-5 shows the X-ray photoelectron results for a Au(111) surface modified under argon atmosphere using a 10 mM solution of 4-nitrothiophenol in dry, degassed N,N-dimethylformamide (DMF) for 48 h. Signals corresponding to the S, C, N elements confirm the deposition on the gold surface of a chemical structure in accordance with the precursor. In the S 2p region, an unresolved doublet is observed at binding energy levels of 162.0 and 163.1 eV for the S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively. These binding energies correspond the gold-thiolate bond. No signal is observed in this region for unbounded sulfur or higher oxidation species of sulfur. Two signals are observed in the C 1s region including 285.4 eV for the C-N and C-S carbons and 284.2 eV for the aromatic carbons. For the nitro group, the N 1s signal is observed at 399 eV, which is typically assigned to the NH$_2$ group due to the reduction of the NO$_2$ group that can result from prolonged X-ray exposure. Due to low signal intensity of the elements in SAMs at short exposure, the exposure time was increased to 28h. The prolonged irradiation time subsequently resulted in conversion of NO$_2$ to NH$_2$ group. This phenomenon has been well studied previously.$^{71,160}$ It has been shown that aromatic-NO$_2$ moieties on the monolayer are very sensitive to X-ray irradiation exposure, which often leads to the reduction of the NO$_2$ to NH$_2$ functional group.
The XPS investigation clearly shows that all excepted elements of the nitrothiophenyl structure are observed. These data are similar to the ones previously observed for the SAMs obtained using the 4-nitrophenyl sulfenyl chloride as a precursor.

4.3-3 PM-IRRAS Characterization

PM-IRRAS was also used to characterize the SAM obtained by modification of Au(111) using 4-nitrophenol. It was particularly helpful in identifying functional groups on the surface. It also provided additional insights into the orientation of the adsorbed thiolate on the Au surface. Figure 4-6b, c shows the structure of the 4-nitrothiophenol using density functional theory (DFT) calculations at the B3LYP level with the 6-311++G(d,p) basis set showing the molecular vibrations and their IR vectors. The optimized structure and the calculated IR spectra are used to determine the main vibration modes. Figure 4-6a shows the PM-IRRAS spectrum of a
Au(111) surface modified using a 10 mM solution of 4-nitrothiophenol in DMF for 48 hours. An intense peak is observed at 1344 cm$^{-1}$, which corresponds to symmetric stretch of NO$_2$ ($\tilde{r}^{\dagger}$NO$_2$). A small peak that appears as a weak shoulder is also observed for the asymmetric stretch of the nitro group ($\tilde{r}$NO$_2$) at 1513 cm$^{-1}$. The intensity of the asymmetric NO$_2$ stretch is markedly lower than its symmetric stretch intensity. The reduction in the intensity of the nitro stretching mode has been previously reported for nitro containing SAMs.$^{2,161}$ The reduction in intensity could be due to temporary change in the direction of the dipole moment in the given mode on the metal substrate, which is perpendicular to the 1,4 molecular axis and does not respond to the polarized light.

**Figure 4-6.** PM-IRRAS spectrum of modified Au (111) on mica using a 10 mM solution of 4-nitrothiophenol in DMF for 48 hours. b and c) Representation of atomic displacements (black arrows) and IR vectors (red arrows) of optimized structure of 4-nitrothiophenol: vibrational modes of the symmetric (b) ($\tilde{r}^{\dagger}$ NO$_2$) and asymmetric (c) ($\tilde{r}$ NO$_2$) stretch modes of the NO$_2$ group.
The PM-IRRAS data suggest a nearly vertical orientation of the adsorbed molecules. These results are similar to the ones previously observed for the SAMs obtained using the 4-nitrophenyl sulfenyl chloride as a precursor.

4.3-4 STM Investigation

STM was used to characterize the structure of the obtained 4-nitrophenylthiolate SAM using the 4-nitrothiophenol as precursor. Figure 4-7 shows various resolutions of STM images of a Au (111) surface modified with 10 mM 4-nitrothiophenol in DMF for 48 hours. These images provide detailed information about the structure of the modified surface. The efficiency of the modification method and the extent of the modification on the surface can be assessed by the large-scale images obtained by the STM. Sub-molecular details and long-range ordered domains can be observed on Au surface in small-scale images. It is important to note that these images are similar to the ones obtained for SAMs prepared with the 4-nitrophenyl sulfenyl chloride.²
Figure 4-7. STM images of a Au(111) surface in air, modified using 4-nitrothiophenol (10 mM in DMF) for 48 h. (a) 30 × 30 nm² and (b) 12 × 12 nm². Tip bias = 0.1 V, tunneling current (0.1 - 0.4 nA) and scan rate (4.8 lines/s).

For the well-ordered phase (Figure 4-8) two lattice vectors (a = 4.99 ± 0.15Å and b = 4.97 ± 0.19 Å) were used to describe a unit cell. The angle between them measured as (α = 61.01 ± 2.02°). The dimensions of the unit cell are similar to the √3 x √3 structure typically observe for aliphatic SAMs. This molecular density implies excellent molecular packing between the aromatic moieties. The SAMs obtained from 4-nitrothiophenol as a precursor are markedly robust and the STM images were stable and reproducible using a wide range of tunneling conditions (0.1 to 0.4 nA).
Figure 4-8. STM images of a Au(111) surface in air, modified using 4-nitrothiophenol (10 mM in DMF) for 48 h. (a) 12 x 12 nm$^2$, (b) 3 x 3 nm$^2$, (c-d) Height profiles along line A and B. Tip bias = 0.1 V, tunneling current = 0.2 nA and scan rate = 4.8 lines/s.

As discussed before, obtaining long-range-ordered aromatic SAMs specifically in the case of substituted aromatic thiols as precursors is challenging. For example, STM images of SAMs obtained using halogen-substituted thiophenol by Jiang et al$^{162}$ and Wong et al$^{163}$ showed that molecules self-assemble only into low-coverage ordered phases. They concluded that molecules are more inclined to lay down toward the gold surface. Similarly, STM investigation
of 4-nitrophenyl thiolate SAMs in solution by Kolb et al.\textsuperscript{164} also showed lower coverage with small domains of ordered structures together with unordered phases. To our knowledge, our investigation is the first report of high density aromatic SAMs obtained using 4-nitrothiophenol as a precursor. The robust high coverage, highly packed SAM obtained in the current work revealed the same very unique hexagonal features corresponding to sub-molecular structures observed for the sulfenyl chloride SAMs.

4.3-4a Superstructures and their Dynamics

The most interesting results in this study were provided by the high-resolution STM images (Figures 4-9 and 4-10). These correspond to the unique hexagonal and parallelogram structures observed within the densely packed SAM. These unique features were only observed once before for SAMs prepared using the 4-nitrophenyl sulfenyl chloride as a precursor in the Houmam group.\textsuperscript{2} They were never observed for aliphatic SAMs. The unique hexagonal structures contain a central bright spot distinguished from the surrounding spots. Line profiles drawn, in various directions, through the brighter spots, located at the center of the hexagonal structures, show that these molecules are standing higher compared to other surrounding molecules (Figure 4-9). The line profiles drawn across these brighter spots in different directions also revealed that the distance of these brighter spots and the adjacent molecules are 5 Å. This observation, regardless of what has been actually observed by STM (S or terminal group) shows that each spot represents a single molecule on the surface. As a result of these observations, and like for the 4-nitrophenyl sulfenyl chloride SAM,\textsuperscript{2} it is suggested that the height differences among molecules can be due to the presence of adsorbed molecules with different twist or tilt angle, which may bring the molecules or atoms to slightly different heights.
The current results are very important because they provide support to the previous studies in the Houmam group regarding the origin of the brighter spots as nearly vertical oriented molecules compared to the rest of the adsorbed molecules in the 4-nitrophenelthiolate SAM using a different precursor.\textsuperscript{2} It is worth noting that this was only possible because of the successful optimization of the modification conditions to obtain a higher SAM coverage than what has been reported before despite the huge amount of work on thiols as SAM precursors.

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{fig4-9.png}
\caption{a) STM image of a Au(111) surface modified using 4-nitrothiophenol (10 mM in DMF) for 48 h, 12 x 12 nm\textsuperscript{2}. Tip bias = +0.1 V, tunneling current = 0.2 nA and scan rate = 4.8 lines/s. (b) Line profiles along lines A, B and C over a brighter spot from three different directions.}
\end{figure}

Consecutive STM imaging demonstrates the dynamic nature of the particular molecular structures. Figure 4-10 shows consecutive STM images of the same area taken with a time interval of 48 seconds. In these images, a solid red rectangle represents a hexagon structure that
transforms to the regular $\sqrt{3} \times \sqrt{3}$ structure and then back to a hexagonal structure in sequential images of a defined area. Another interesting finding is the formation of de novo structures such as parallelograms as seen in Figure 4-10 (white and yellow rectangles). A hexagon appears to be transforming into a parallelogram and turn back into hexagon in the subsequent images of the same area. A plausible explanation is that all spots regardless of their darkness and brightness represent the same adsorbed molecule and variation in the brightness of the spots and surface features might reflect the arrangements and rearrangements of the molecules on the surface. These findings reinforce the theory of dynamic molecules on highly packed SAM.
Figure 4-10. Consecutive STM imaging of a SAM of 4-nitrothiophenol on Au(111). 12 × 12 nm². Images are taken in the sequence a-d. Tip bias = +0.1 V, tunneling current = 0.2 nA and scan rate = 4.8 lines/s.

4.3-4b Origin of the Superstructures

Further analysis of the STM images with focus on the superstructures can provide a better insight to the origin of these structures. The length of several hexagons edges are about 5 Å consistent with expected dimensions of hexagonal structure. Figure 4-11b-g show line profiles along all edges of the hexagons. Interestingly three peaks are readily visible along the edge of the
hexagons. Two observed peaks are ~2.20-2.33 Å apart from each other and the third peak located at a slightly longer distance (~2.79-2.87 Å). All edges of the hexagon are almost identical in length indicating thus the two peaks in a line profile must be representing a single molecule. We already knew that the hexagon is composed of six individual molecules with an extra molecule in the middle. A very mild filtering (levelling and smoothing) applied to the STM image to reduce the noise (Figure 4-11d) leads to further characterization of the hexagons, showing 12 spots consistent with the extracted line profiles.

In order to understand the origin of these 12 spots, we calculate the distance between two oxygens of nitro group in an optimized structure of the parent molecule at the B3LYP level at 2.18 Å. This value is close to the one obtained from the line profile for each edge of the hexagon in the STM images. This reconfirms the suggestion, made in the investigation of the 4-nitrophenylsulfenyl chloride, that these spots represent the oxygen atoms of the NO₂ groups. Therefore, the 12 observed spots arise from a special arrangement of the adsorbed molecules. In order to locate two spots representing two oxygen atoms of the terminal nitro group along the edge of the hexagon, the molecule should be angled in such a way that one of the oxygen atoms aligns with the sulfur atom of the same molecule (Figure 4-12c). Figure 4-12e,f show a schematic top view of this structure. In this case STM sees each individual molecule as two spots.
Figure 4-11. STM image of a Au(111) surface modified using 4-nitrothiophenol showing a hexagon structure. Scan size: (3 x 3 nm$^2$). (b) to (g) Line profiles along six edges of the hexagon as marked in a.
Figure 4-12. a) STM images of a SAM of 4-nitrothiophenol on Au(111). 12 × 12 nm². b) Height profile along line A. c) optimized structure of p-nitrophenyl thiolate along with its top view. d) STM image showing a hexagon (scan size: 3 × 3 nm²). e) Schematic representation of the molecular rearrangement providing the hexagonal structure. (Reprinted with permission from reference 2). f) Top view schematic structure of 4-nitrophenyl thiolate molecules on the Au(111) surface. Tip bias = +0.1 V, tunneling current = 0.2 nA and scan rate = 4.8 lines/s.

Aside the predominantly observed hexagons, STM images also show parallelogram structures that originate, as previously discussed, from a certain molecular arrangement that can reversibly reform the hexagonal structure. Figure 4-13 illustrates the STM image and line profiles for a parallelogram structure. Like the hexagonal structure, line profiles drawn along four edges of the parallelogram show three distinct peaks with two peaks closer to each other than the third one. A model for the formation of the parallelogram is suggested in Figure 4-13b,c.
**Figure 4-13.** a) STM images of a Au(111) surface modified using 4-nitrothiophenol showing two parallelogram structures. d-g) Line profiles along the parallelogram edges. b) Schematic representation of the molecular rearrangement providing the parallelogram structure. (Reprinted with permission from reference 2). c) Top view schematic structure of 4-nitrophenyl thiolate molecules on the Au(111) surface. Tip bias = 0.1 V, tunneling current = 0.2 nA and scan rate = 4.8 lines/s.

As discussed before, the long profiles going through the brighter spots in the middle of each hexagon in Figure 4-9b and Figure 4-12b show that these spots are standing higher than the rest of the molecules. Based on the proposed structure for the hexagons and knowing that the central spots interact equally with all the six molecules in the hexagon, it was suggested that these central brighter spots represent vertically absorbed molecules while the remaining molecules are slightly tilted. This finding is supported by the PM-IRRAS data that demonstrated
that the molecules are less tilted on the surface. This has been achieved by measuring the
difference of intensity between symmetric and anti-symmetric NO\textsubscript{2} stretches. Figures 4-12e, f
show the proposed model for the SAM on gold where a hexagon is surrounded with a $\sqrt{3} \times \sqrt{3}$
phase. Besides resolving the orientation of molecules on the surface, these data suggest that not
only STM shows a high packed aromatic thiolate SAM on gold substrates but also that it is
capable of visualizing the atomic resolution. These STM images provide new explanations and
raise new questions for a heavily debated fundamental aspect in STM. For example, why certain
molecules appear as individual spots and others are involved in creating superstructures such as
hexagons, and parallelograms? And why the molecules are dynamic on the surface and convert
from one form to another?

It has been shown that the surface stress would be larger for structure whose molecular
density is higher compared to lying-down phase.\textsuperscript{165} Thus based on current results and the
observations published by Houmam \textit{et al.}\textsuperscript{2} the presence of distinct features and rearrangements
on the surface of aromatic SAMs with high molecular coverage are most likely the result of
SAM stress. This stress may arise from the lattice mismatch between an adsorbate layer
(aromatic moiety) and the substrate that can be released by increasing or decreasing the distance
between adsorbate molecules, which subsequently led to the alteration in arrangement of certain
adsorbed molecules. It is logical to suggest that molecules that are involved in making the
particular structures (hexagons and parallelograms) are in a frozen state allowing for the sub
molecular details to be observed. There are other bright spots that are not involved in formation
of these structures. These bright spots may be more dynamic, with slight twisting around the
molecular axis.
Previous STM studies in the Houmam group, using 4-nitrophenyl sulfenyl chloride as a precursor, provided the initial thought about this hypothesis. Low (showing mainly a row based $4 \times \sqrt{3}$ phase) and high (showing a $\sqrt{3} \times \sqrt{3}$ hexagonal phase) coverage aromatic SAMs, using two different modification conditions, were reported in the STM images. The superstructures were exclusively observed in the high coverage SAMs. The present study provides support for these initial investigations as it confirms, using a different precursor, that (i) highly packed SAMs, higher than what has been previously reported, can indeed be obtained using aromatic thiols, (ii) the same unique structures, hexagons and parallelograms, are observed for the 4-nitrophenyl thiolate SAMs as seen with the sulfenyl chlorides as precursors, and (iii) that submolecular details are observed by STM for the NO$_2$ terminal group for these SAMs. This last result is particularly important and helps understand the origin of the bright spots, corresponding to adsorbed molecules, in STM images of standing-up SAMs.
4.4 Bis(4-nitrophenyl) Disulfide as a Precursor for the Modification of Gold Surfaces

The bis(4-nitrophenyl) disulfide was investigated in the same manner as the 4-nitrothiophenol. Both polycrystalline gold electrodes as well as Au(111) surfaces were used. Various conditions were tested but the SAMs obtained with this precursor were of much lower quality than those obtained for the parent thiol. Here we report the results for the modification conditions that showed the highest coverage.

4.4-1 Stripping CV Results

Reductive stripping voltammetry provided initial evidence for the successful modification of polycrystalline gold electrodes using bis(4-nitrophenyl) disulfide as a precursor. The gold electrodes were prepared as previously described for the 4-nitrothiophenol (see section 4.3-1). The modification was performed in a 10 mM solution of bis(4-nitrophenyl) disulfide in DMF. The reductive stripping was performed in a 0.5 M aqueous KOH solution at different modification times, the results of which are presented in Figure 4-14.

A reductive stripping peak (-0.89 V vs SCE) is observed at modification time of 10 min for the 1st scan and a response similar to the bare gold is observed for the 2nd scan for the modified solid polycrystalline gold electrode. The area under the stripping peak increases from 10 min to 10 h modification time and remains constant at longer modification times up to 18 hours.

Figure 4-15 shows a time dependent coverage, calculated using the method described in section 4.3-1. The measured desorption charges indicate that the disulfide based monolayers have much lower packing density compared to the ones prepared using the parent thiol. The calculated surface coverage increased from ~0.035 ML for a 10 minutes modification time to
0.111 ML for a 10 h of modification time. No coverage increase was observed beyond the 10 h modification time and the maximum coverage value was indeed 0.111 ML, a lot lower than the value found with the 4-nitrothiophenol as a precursor (0.33 ML).

Similar observations have been reported previously in the literature. For example, electrochemical and second harmonic generation (SHG) experiments showed that the rate of adsorption on gold surfaces for disulfides is about 40% slower than thiols. 55,166 Hager et al. reported different behaviors for the adsorption and desorption of a thiol and a disulfide at an Au(111) single crystal electrode. 167

![Figure 4-14](image)

**Figure 4-14.** Time dependent cyclic voltammetry, in a 0.5 M aqueous KOH solution at 25 °C, of a 2-mm diameter solid gold electrode modified with bis(4-nitrophenyl) disulfide.
Figure 4-15. Time dependent coverage of the deposited monolayer calculated from the reductive stripping voltammetry of previously modified polycrystalline solid gold electrodes in a 0.5 M aqueous KOH solution at 25 °C.

These results show already that while the modification of polycrystalline gold electrodes is feasible using bis(4-nitrophenyl) disulfide, the coverage is very low, and the expected SAM structure is not a highly packed phase as observed with the 4-nitrothiophenol and before with the 4-nitrophenyl sulfenyl chloride.

4.4-2 XPS Characterization

Figure 4-16 shows X-ray photoelectron results for a Au(111) surface modified using a 10 mM solution of bis(4-nitrophenyl) disulfide in dry, degassed DMF for 48 h under nitrogen atmosphere. An unresolved doublet for the S 2p region is observed at binding energies of 162.0 and 163.2 eV for the S 2p3/2 and S 2p1/2, respectively that is representative of gold-bound thiolate species. Absence of the intact S - S bond signal confirms that the chemisorption of the disulfide proceeds with dissociation of the S - S bond.13 Two signals are observed in the C1s region
including 285.5 eV for the C-N and C-S carbons and 284.3 eV for the aromatic carbons. The N1s peak observed at 399 eV originates from the amino group (see section 4.3-2 for details).

**Figure 4-16.** XPS spectra of the sulfur, carbon and nitrogen regions of Au(111) on mica modified using a 10 mM solution bis(4-nitrophenyl) disulfide in dry, degassed DMF for 48 h under nitrogen atmosphere.

4.4-3 PM-IRRAS Characterization

Au(111) substrates on mica were modified with a 10 mM concentration of bis(4-nitrophenyl) disulfide in DMF for 48 hours. PM-IRRAS analyzes of these samples did not show any peak for NO$_2$ in either symmetric or asymmetric stretching mode. Absence of the NO$_2$ signal is suggestive of parallel orientation of the nitro functions in relation to the surface. In other word the vector in this mode shows parallelism to the Au surface and therefore it will not respond to IR irradiation. These results are in agreement with the ones obtained with stripping voltammetry and
further support the formation of a lower density monolayer using bis(4-nitrophenyl) disulfide as a precursor.

4.4-4 STM Investigation

Figure 4-17 shows STM images of a modified Au(111) substrate using a 10 mM solution of bis(4-nitrophenyl) disulfide in DMF for 48 hours. While the thiol modification gives a high coverage SAM, the disulfide one leads only to a very low coverage SAM, under the same experimental conditions. In this study STM images show areas of small domains with ordered structures next to areas of unordered phases as seen on Figure 4-17a.

In the ordered phase (Figure 4-17b) the adsorbed molecules are organized into parallel stripes, separated by a distance of 8.51 Å ± 0.45 Å (Line B) and each stripe comprised of molecules that are 4.74 ± 0.25 Å apart from each other (Line A) suggesting a much lower density of molecules on the surface compared to 4-nitrobiophenol precursor and previously in our group with the 4-nitrophenyl sulfenyl chloride. Assuming that each bright spot is ascribed to an individual 4-nitrothiophenolate molecule, these dimensions reveal a 3 x √3 structure. The proposed structural model containing a 3 x √3 unit cell is shown in Figure 4-17c.
Figure 4-17. Unfiltered STM images of a Au(111) surface in air on mica modified using bis (4-nitrophenyl) disulfide (10 mM in DMF) for 48 h. (a) 40 × 40 nm², b) 9 × 9 nm², c) Proposed structural model for the 4-nitrophenylthiolate SAM on Au(111). Bias (0.1 V) tunneling current (0.8 nA) and scan rate (4.8 lines/s).

A number of explanations can be suggested for the lower coverage and striped phases observed in the case of disulfide SAMs.

- Sterically, approach of the S2 moiety of the disulfide to the surface is likely hindered particularly when they are attached to the bulky substituted ring.
- The adsorption of the disulfide is likely to occur on different sites at Au(111) than that of the thiol with larger tilt angle.\(^{168}\)

In addition to the STM images, data obtained from other characterization techniques including PM-IRRAS and CV collectively provide strong support for the low coverage of disulfide SAM and show that the adsorbed aromatic thiolates are likely much tilted compared to those standing up in the SAMs obtained from 4-nitrothiophenol and previously from the 4-nitrophenyl sulfenyl chloride.\(^{67}\)
Chapter 5. Summary and Future Work

5.1 Summary and Conclusion

The main purpose of this thesis is to provide further evidence into heavily debated issues regarding the origin of the various features and ability of STM to image atomic resolution. Previous studies on STM images obtained from 4-nitrophenyl sulfenyl chloride SAM on Au(111) provided a unique insight into arrangement of molecules and for the first time demonstrated that the STM is capable of visualizing sub-molecular details. Despite this strong proof of principal, the ability of STM to uncover the sub-molecular details of SAM remains elusive. In order to gain more insight into the nature of the information that is gathered by STM from the surface and to assess the ability of STM to unravel sub-molecular details, we studied the SAMs attained by two nitro-substituted precursors (4-nitrothiophenol and bis (4-nitrophenyl) disulfide) on gold surfaces using various characterization techniques including CV, XPS, PM-IRRAS and STM. Obtaining long-range-ordered aromatic SAMs are more challenging in comparison to aliphatic SAMs. It is important to overcome the limitations including low packing densities and irreproducibility specifically in aromatic thiols that also undergo oxidation to disulfides and sulfonates in solution as well as surface. In this study a wide range of modification conditions have been used to achieve high coverage SAMs.

Using 4-nitrothiophenol lead to the successful formation of highly ordered and densely packed aromatic SAMs on Au(111) and polycrystalline solid gold electrodes under controlled modification conditions. Reductive stripping voltammetry was used as straightforward technique to assess the modification of a polycrystalline gold where the reduction of the nitro group was observed along with the desorption of the monolayer. Area under reductive peak also revealed
the high surface coverage. XPS analysis of the modified surface revealed successful formation of monolayer and signals associated with all elements (C, N, S) were detected. This is further supported by using PM-IRRAS technique that identified the functional group and provided further evidence for the nearly vertical orientation of the precursor molecules on the surface. STM has shown the formation of closely packed and highly ordered aromatic SAMs on Au(111) corresponding to a $\sqrt{3} \times \sqrt{3}$ hexagonal phase with an area per molecule of $\sim$21.4 Å$^2$ that this study, to our knowledge is the first report of high density aromatic SAM obtained with this precursor. Beside the main hexagonal lattice, the same unique structures, hexagons and parallelograms, are observed for the 4-nitrophenyl thiolate SAMs as seen with the sulfenyl chlorides as precursors and that sub-molecular details are observed by STM for the NO$_2$ terminal group for these SAMs.

In order to provide more evidence for the origin of superstructures observed by STM, bis (4-nitrophenyl) disulfide has been selected as another representative of the nitro terminated aromatic SAM family. It was expected to obtain similar monolayer, with the same properties as the SAM prepared from its corresponding thiol. Even through XPS spectra confirmed that both thiol and disulfide precursors form chemically similar monolayer (thiolate-gold bond), however data obtained from other techniques such as CV, and STM revealed a much lower quality SAM. The lack of NO$_2$ signal in PM-IRRAS analyzes strongly suggest that molecules are more inclined to lie down on the Au(111) surface and therefore IR is not able to show even the asymmetric stretch mode of NO$_2$. STM images show relatively short-range domains with ordered structure and no evidence for the presence of superstructures. For the well-ordered phase, a unit cell of $3 \times \sqrt{3}$ structure can be deduced. Comparing the thiol and disulfide derived SAMs, revealed that superstructures were only observed in densely packed SAMs obtained from 4-nitrothiophenols.
Similar results previously reported by Houmam et al. using nitrophenyl sulfenyl precursor at low and high coverage, using two different modification conditions. So, it is plausible to conclude that the presence of distinct features and rearrangements on the surface are most likely induced from the SAM stress so It is logical to suggest that the molecules involve in formation of a particular structures (hexagons and parallelogram) are in a frozen state allowing for the sub-molecular details to be observed. This study in conjunction with the previously published research provide stronger evidence into the long-standing question regarding the ability of STM to image sub-molecular details of the molecules.

5.2 Future Work

In this study, we investigated the STM contrast of nitro-terminated aromatic SAMs. In conjunction with previously published studies, we suggested that STM is capable of providing atomic resolution. For example, in our work we could suggest that STM is visualizing the two oxygen atoms in the terminal NO$_2$ group of aromatic SAM. More studies required in order to fully understand the nature and the origin of the STM contrasts. This can be explored further by utilizing different precursors with nitro terminal group or STM study of similar SAMs with monoatomic tail groups (e.g. Cl, Br etc.) under different imaging conditions.

Fabrication of well-defined organic surfaces with specific properties received a lot of attentions. Within the wide library of functional groups −NO$_2$ has been widely employed for post-modification of SAMs due to its ability to couple with other compounds. Electron withdrawing capability, sensitivity of the nitro group towards different irradiation sources and easily converting to primary amine functions (−NH$_2$) make nitro terminated SAMs practical in the fields of electronic, biology and lithography purposes.
For example, SAMs from nitro-terminated group have been used to create biocompatible surfaces with the ability to transform nitro groups (−NO2) into primary amine that can be subsequently bioconjugate with proteins on the surface.

So, as an extension of this project, the formation of well-ordered nitro-terminated aromatic SAMs can provide the foundation for the post-modification procedures such as chemical post-modifications and scanning electrochemical microscopy techniques.
REFERENCES


30. McGuiness, C. L. *et al.* Molecular self-assembly at bare semiconductor surfaces: Preparation and characterization of highly organized octadecanethiolate monolayers on


56. Taubert, C. E. Influence of Different Additives on the Copper Electroplating onto Au (111) and Cu (111) Substrates. (2006).


86. Stettner, J. Self assembled monolayer formation of alkanethiols on gold: Growth from solution versus physical vapor deposition. 1–139 (2010).


95. Gao, J. Structural analysis of self-assembled monolayers on Au (111) and point defects on HOPG. 189 (2013).


102. Cunha, F. & Tao, N. J. Surface charge induced order-disorder transition in an organic


127. Zhong, C., Zak, J. & Porter, M. D. Voltammetric reductive desorption characteristics of alkanethiolate monolayers at single crystal Au (111) and (110) electrode surfaces. 421, 9–13 (1997).


